

STRUCTURAL PECULIARITIES AND SOME ELECTRICAL-AND-PHYSICAL PROPERTIES OF BISMUTH OXIDE AND ANTIMONY TRICHLORIDE AND TRIBROMIDE

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ABSTRACT

The systems of antimony oxide (III) – antimony chloride (III), antimony oxide (III) – antimony bromide бромид (III), bismuth oxide (III) – bismuth chloride (III) and bismuth oxide (III) – bismuth bromide (III) are the sections of the triple systems metal - oxygen - halogen. In the present report there is considered the information found in literature of the phase diagrams of binary systems components: metal – oxygen, metal – halogen – and literature data of methods of obtaining, structures and properties of the compounds in the systems. The analysis of the elementary cells parameters permitted to suppose their laminated structure and to build these compounds structures models. By the NQR method there was established the absence of the inversion center in some bismuth oxo-halogenides (by the presence of piezoelectric resonance lines) and revealed a significant dependence of NQR spectra transitions intensity on weak magnetic fields.

From the practical point of view the interest presents further studying of crystal structures and physical properties of some bismuth oxo-halogenides, as due to the defect oxygen sublattice they can appear to be efficient solid electrolytes.

INTRODUCTION

For the first time crystal structure of α – Bi_2O_3 modification was defined by Sillen [1, 2] according to Weisenberg's X-ray photographs. Bismuth atoms position were defined from the analysis of interatom function of Paterson and of oxygen atoms – from space considerations. Repeated studies confirmed the positions of the two oxygen atoms and verified the position of the third oxygen atom [3, 4]. α – Bi_2O_3 structure presents a layer of bismuth atoms, parallel planes y o z at $x = 0$ and $x = 0,5$, which are divided by oxygen atoms layers at $x = 0,25$ and $x = 0,75$. Around bismuth atoms there are located five or six oxygen atoms. In both cases coordination polyhedron can be described as distorted octahedron [2]. In the structure there are a number of voids parallel to 'c' axis. In work [3] there was established the connection of α – Bi_2O_3 structure with the distorted defect structure of fluorite type δ – Bi_2O_3

In work [1] there was studied the cubic phase with the elementary cell parameters $a = 5,525 \cdot 10^{-1} \text{ Nm}$ obtained by hardening. The author considers that its structure is connected with the fluorite structure but has ordered defects in oxygen sublattice in the direction $\langle \text{III} \rangle$ (Fig. 1).

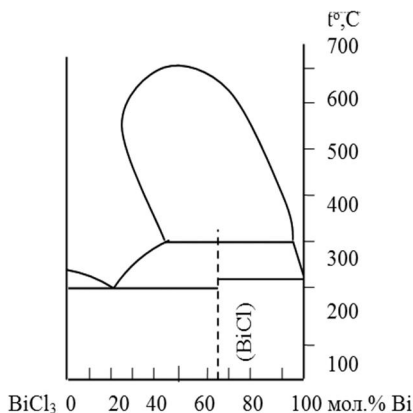


Fig.1 – System fusibility diagram

β – Bi_2O_3 . Metastable tetragonal modification was obtained by sedimentation on the cold base of Bi_2O_3 spray which was formed at oxygen passing through metal bismuth melt and thin layers of melted bismuth oxide hardening (III). On the basis of studying X-ray photographs of the powder there was selected space group $P4_2m$. The authors of [6] obtained fine crystals of p-modification by means of pouring bismuth salts solutions into the boiling solution of potassium hydroxide or caustic soda. X-ray structural analysis of the crystals permitted to verify the ‘a’ parameter and space group of β – modification. The results of the work are confirmed in [4] by X-ray photographs and in [5] electrographically. According to the data β – Bi_2O_3 structure supposes the possibility of significant composition variation by oxygen (from Bi_2O_3 to $\text{Bi}_2\text{O}_{3.5}$). Other authors suggest the formula of β – modification to be $\text{Bi}_2\text{O}_{2.5}$ [1, 2, 4].

γ - Bi_2O_3 . Metastable γ - modification of bismuth oxide (III) crystallizes in the cubic volume-centered lattice (table 4) and is isostructural to the large group of compounds formed by bismuth oxide (III) with many metals oxides Al, Si, Fe, Ti, Zn, Ge, Ce, Pb and many others) called “sillenites” or “sillenite-phases” [4] (by the name of L. Sillen who was the first to study $\text{Bi}_{12}\text{SiO}_{20}$ phase). In the case of tetravalent metal oxide the formula of the compound is $\text{Bi}_{24}\text{MeO}_{40}$, as a rule, and in the case of trivalent iron and bivalent zinc oxides they are $\text{Bi}_{24}^{3+}\text{Bi}_5^{5+}\text{Fe}^{3+}\text{O}_{40}$ и $\text{Bi}_{36}^{3+}\text{Bi}_2^{5+}\text{Zn}^{2+}\text{O}_{60}$, respectively [5]. The parameter of the elementary volume-centered cell, sillenite phases depends on metal ion radius and lies in the limits of 10, 10-10, 27 10^{-1} Nm.. The parameter maximum value corresponds to pure γ -modification of bismuth oxide. The determination of $\text{Bi}_{12}\text{GeO}_{20}$ structure [5] showed that germanium atoms are located in tetrahedron voids formed by oxygen atoms and have coordinates (000) и (1/2 1/2

Space group $Pn3m$. On the basis of electronic-and-graphic studies in work [1] there was made a conclusion that the elementary cell must be volume-centered because bismuth and oxygen atoms take private positions answering the conditions of extinguishing $h+k+l=2n$. The authors of [1] suggested the model of the structure δ -modification of bismuth oxide (III) (Fig.1), in which bismuth atoms are located in the nodes of the cubic face-centered cell and oxygen atoms statistically take the centers of six (from eight) octants.

1/2). Atoms coordinates determination for γ - Bi_2O_3 showed significant increase of oxygen tetrahedrons dimensions at (000) and (1/2 1/2 1/2), which is conditioned by the bismuth atoms increase (almost two times) as compared to germanium atoms [4]. Coming from the structural considerations the authors of [5] suggest in the case of pure γ -modification the formula $\text{Bi}_{25}^{3+}\text{Bi}^{5+}\text{O}_{40}$. Such a formula with the ordered places of atoms Bi^{3+} - (000) and Bi^{5+} - (1/2 1/2 1/2) is useful in energy (20 J/mol) [4]. The necessity to keep oxygen in the atmosphere during two hours at 800-820°C of the bismuth oxide (III) sample for obtaining pure γ -modification indirectly confirms the formula suggested in [5]. However it's necessary to notice that in spite of the large number of works relating to bismuth oxide (III) polymorphism, the presence of pentavalent bismuth in γ - Bi_2O_3 structure is nor confirmed experimentally and requires to be proved.

It's interesting to notice that many representatives of sillenites class possess perspective electro-physical properties such as piezo- and photoelectrical, electrical and acoustic and optical ($\text{Bi}_{24}\text{Si}_2\text{O}_{40}$, $\text{Bi}_{24}\text{Ge}_2\text{O}_{40}$, $\text{Bi}_{24}\text{Ti}_2\text{O}_{40}$) [5]. From the publications it's also known that bismuth oxide (III) is a semiconductor and the conductivity type (p or n) depends on temperature and oxygen partial pressure.

BISMUTH-CHLORINE AND BISMUTH-BROMINE SYSTEMS

In publications there is information about BiCl_3 - Bi system obtaining by means of thermal analysis [6] and by visual observations. In all the cases there were built fusibility diagrams. In Fig. 2 there is shown a diagram obtained in the work and coinciding with the data of [6]. In the system there was revealed the presence of bismuth monochloride (I) BiCl . The eutectic between bismuth trichloride and monochloride is such that it has in the composition about 29 at.% of bismuth and melts at 202°C, and between monochloride and metal - at 267°C [7]. Bismuth monochloride melts with decomposing into two liquid phases at 320°C. In the composition ranges 45-95 at.% of bismuth and temperatures 320-780°C in the system there is observed stratification in the liquid phase. In work [6] there is reported about an individual bismuth chloride (I) emission from the reaction mixture of bismuth trichloride with metallic bismuth by means of excess BiCl_3 distillation at 180°C in vacuum or by means of extracting this excess with benzene. Bismuth monochloride presents a diamagnetic powder of black color, stable in air at ambient temperature. Structural studies showed that bismuth monochloride crystallizes in a rhombic syngony with the parameters of an elementary cell $a = 23,057$, $b = 15,040$, $c = 8,761 \cdot 10^{-1}$ Nm and has the formula $\text{Bi}_{12}\text{Cl}_{14}$.

Studying the system BiBr_3 - Bi was carried out in works [6, 7, 8]. The view of the diagrams obtained by the authors coincides with each other and is analogous to the fusibility diagram of BiCl_3 - Bi system. In BiBr_3 - Bi system there was also revealed the existence of bismuth monobromide melting at

294°C [7]. Eutectic between bismuth bromides (10) and (I) has in its composition 21 mol% of bismuth and melts at 205°C, between BiBr and metallic bismuth - 98,7 mol.% of bismuth and melts at 263°C [7]. In the system there is observed the region of stratification in the liquid phase in the composition ranges 57,4-98 mol.% of bismuth and temperatures 294-538°C. In the composition ranges 0-66 mol.% of bismuth at 158°C there is observed a phase transfer $\alpha \rightarrow \text{BiBr}_3 \rightarrow \beta - \text{BiBr}_3$ [7]. Thus, it can be considered that in the publications there are reliable data about bismuth-chlorine and bismuth-bromine systems.

STRUCTURE AND SOME PROPERTIES OF BiCl_3 AND BiBr_3

The crystal structure of bismuth trichloride was studied in [8]. The data of the primary X-ray structural analysis are given in *table 1*. The crystal lattice of bismuth trichloride is molecular. Bismuth atoms have three neighboring chlorine atoms at the distance about $2,5 \cdot 10^{-1}$ Nm and five atoms of halogens are located farther (about $3,2 \cdot 10^{-1}$ Nm) [8]. On the whole the coordination polyhedron of bismuth atoms can be described as trigonal prism with six chlorine atoms in the apexes and two chlorine atoms outside of the prism two side faces. In the publications there are described two modifications of bismuth tribromide [9]. Low temperature α -modification is stable at lower than 158°C and has a molecular lattice (table 1). High temperature β -modification exists at higher than 158°C and is isostructural to aluminium trichloride [9]. In the coordination structure $\beta - \text{BiBr}_3$ each bismuth atom is surrounded by six bromine atoms at the distance $2,82 \cdot 10^{-1}$ Nm. β -tribromide of bismuth is the only trihalogenide of Y_B group having a coordination structure. In work [9] there were compared structural data for all antimony and bismuth trihalogenides.

Steam pressure over bismuth trichloride was studied by a statistical method in [6]. There was shown that the steam over bismuth trichloride consists of monomer molecules of BiCl_3 . In the same work we can find references to other authors' works relating to steam pressure and composition over bismuth trichloride. Bismuth tribromide and trichloride melting temperatures are 218 and 230,5°C, respectively [9].

Table 1 –X-ray data for bismuth chloride and bromides (III)

| | Chloride [7] | α - bromide [8] | β - bromides [9] |
|---|-------------------------------------|---|--|
| Syngony | rhombic | monoclinal | monoclinal |
| Space group | Pn2 ₁ a | Pn2 ₁ /a | C2/m |
| Cell parameters 10 ⁻¹ nm and degree | a = 7,641 b = 9,172 c = 6,291 | a = 8,429 b = 9,848 c = 6,756 β = 109,65 | a = 7,249 b = 12,528 c = 6,849 β = 110,68 |
| Number of form.units | 4 | 4 | 4 |
| ρ_{form} , g/cm ³ | 4,75 | 5,79 | 5,12 |

Of bismuth trichloride and tribromide chemical properties there is worth mentioning their special hygroscopicity and tendency to hydrolysis in the result of which there are formed oxo-halogenides of compositions BiOCl и BiOBr [17].

BISMUTH OXIDE (III) SYSTEMS

There was not found any information about system studying the systems of bismuth oxide (III)-bismuth chloride (III) and bismuth-bromide (III) in publications. Oxo-halogenides of the simplest compositions BiOCl and BiOBr are obtained in hydrolysis of a corresponding bismuth trihalogenide [4,5] and crystallize into a structural type PbFCl of tetragonal syngony (*table 2*). The crystal structure of these oxo-halogenides is characterized by brightly expressed stratified structure [10].

The authors of [4] worked out a method of obtaining monocrystals BiOCl and BiOBr by means of growing from the steam with the help of chemical gas-transporting reactions. There were obtained thin plate crystals with the area 1 cm^2 . On the monocrystals there were studied such properties as heat-conductivity, energy spectrum of adhesion levels, two-phonon absorption, affect of compression and electrical field on the absorption strip edge [6], luminescence and energy levels, photo-emission properties and dispersion interference studies of refraction index and the analysis of direct and indirect transfers [7]. In work [10] there were obtained and interpreted in the terms of group theory spectrum G and combination scatterings in frequency ranges $40\text{-}600 \text{ cm}^{-1}$ and in [9] in frequency ranges $50\text{-}205 \text{ cm}^{-1}$.

The authors of [10] using electronic microscopy studied the affect of growth conditions on the crystal structure and crystal morphology of bismuth oxo-chloride BiOCl .

Standard enthalpy and entropy of crystal bismuth oxo-xhloride was determined by EDS method in [8].

The authors of [9] studied the spectra of nuclear quadrupole resonance of BiOCl , BiOBr and on the basis of molecular orbitales theory there were explained the laws of changing the constants of quadrupole tie.

By the method of thermo-gravimetry there was studied thermal stability of BiOCl и BiOBr . The compounds begin decomposing at 720 and 620°C , respectively. The final product of thermolysis in the both cases is bismuth oxide (III). The compositions of bismuth oxo-chlorides and oxo-bromides different from BiOX there are described in the publications such as $\text{Bi}_7\text{O}_9\text{Cl}_3$, $\text{Bi}_{24}\text{O}_{31}\text{X}_{10}$ (where $\text{X} = \text{Cl}, \text{Br}$) and $\text{Bi}_{12}\text{O}_{15}\text{Cl}_6$. $\text{Bi}_7\text{O}_9\text{Cl}_3$ phase was obtained in the form of pale-yellow needle crystals by means of heating BiOCl in air at 600°C .

The conclusion about the compound forming was made only on the basis of the chemical analysis, that's why the existence of such composition of bismuth oxo-chloride cannot be considered finally established.

Table 2 –X-ray graphic data for bismuth (III) oxo-halogenides

| Oxo-halogenide | Syngony | Space group | Elementary cell parameters in 10^{-1} Nm, degree. | | ρ exp. g/cm ³ | Z | References |
|---|------------|-------------|---|------------------------------|-------------------------------|---|------------|
| BiOCl | Tetragon. | P4/nmm | a = 3,883 | c = 7,347 | 7,717 | 2 | 7 |
| BiOBr | Tetragon. | P4/nmm | a = 3,915 | c = 8,076 | 8,127 | 2 | 7 |
| Bi ₁₂ O ₁₅ Cl ₆ | Rhombic. | Pnma | a = 40,532 c = 15,487 | b = 3,8688 | 8,14 | 4 | 8 |
| Bi ₂₄ O ₃₁ Cl ₁₀ | Monoclinal | C2/m | a = 9,99 c = 29,44 | b = 3,969 β = 88,77 | 8,20 | 1 | 9 |
| Bi ₂₄ O ₃₁ Br ₁₀ | Monoclinal | C2/m | a = 10,13 c = 29,97 | b = 4,008 β = 90,15 | 8,50 | 1 | 10 |

When heating the mixture of BiOCl and (BiOBr) b Bi₂O₃ in the ratio 1:1 in the sealed quartz ampoules at 800-900°C during several hours the authors obtained some compounds which were prescribed the compositions of Bi₂₄O₃₁Cl₁₀ и Bi₂₄O₃₁Br₁₀ (10:7) according to the data of chemical and X-ray analyses. Bismuth oxide excess formed with quartz a compound Br₄Si₃O₁₂ crystallizing in cubic syngony with the parameter a = 10,27 10^{-1} Nm. In the result of the study there was established that iso-structural Bi₂₄O₃₁Cl₁₀ and Bi₂₄O₃₁Br₁₀ crystallize in the monoclinal syngony (*table 2*). The crystal structure of the compounds resembles the structures of bismuth oxo-halogenides of the simplest composition BiOX. In the lattice Bi₂₄O₃₁X₁₀ alternating bismuth and oxygen atoms form bismuth-oxygen layers between which there are halogen layers.

Bismuth oxo-chloride Bi₁₂O₁₅Cl₆ was synthesized by means of heating the mixture Bi₂O₃ and BiOCl. The product consisted of colorless needle-form crystals extended along the axis "b". In the structure there were found bismuth atoms of both types with the coordination number (by oxygen) four and five. Taking into account non-divided pair of trivalent bismuth elements, coordination polyhedrons of bismuth atoms can be described as four-face pyramid and distorted octahedron. These polyhedrons form bismuth-oxygen network of (Bi₁₂O₁₅⁶⁺) formula passing in zigzag through the structure parallel to the plane XoZ. In the voids of this network parallel to the axis "b" there are located columns of chlorine ions in the form of tri-face prisms. The above-mentioned review of publications on triple systems of antimony-oxygen-chlorine (bromine) and bismuth-oxygen-chlorine (bromine) shows that there was little known about them before our work. In triple systems there are comparatively completely studied only binary components of metal-oxygen and metal-halogen systems. The information about the main systems are limited by the data about individual oxo-halogenide structure obtained by means of hydrolysis of a corresponding trihalogenide. Even for the phases described there are unknown the

regions of thermodynamic stability. Studying some physical properties was carried out only for compounds BiOCl, BiOBr and Sb₄O₅Cl₂. In the systems antimony oxide (III) –antimony halogenide (III) it can be expected analogous to the system antimony oxide (III)- antimony iodide (III) the possibility of existence of oxo-bromides and oxo-chlorides analogous to oxo-iodide Sb₅O₇I, having ferroelastic properties. Besides, it can be supposed that there are must exist oxo-bismuth halogenides with higher content of bismuth than the described Bi₂₄O₃₁X₁₀ (75,6 mol.% Bi₂O₃). In the system bismuth oxide (III)-bismuth iodide (III) there was found oxo-iodide of the composition Bi₅O₇I (87,5 mol.% Bi₂O₃). The question of the possibility of halogenides stabilizing affect on high temperature metastable modifications of bismuth oxide (III) is still unclear (particularly the possibility of sillenite phases forming).

STRUCTURE AND PROPERTIES OF ANTIMONY TRICHLORIDE AND TRIBROMIDE

Antimony trihalogenides molecules in the gaseous state have trigonal-pyramidal configuration, and metal atom in the pyramid apex. The interatom distances are: Sb – Cl 2,352; Sb – Br 2,52 (10⁻¹Nm), and valent angles Halmet-Hal are 99,5 and 96° for chloride and bromide, respectively [11]. X-ray graphical studying trichloride [12] and two antimony tribromide modifications [13, 14] showed that monomeric molecular structure with trigonal pyramidal configuration maintains in crystal condition, which provides relatively low melting temperatures of halogenides. Both chloride and two antimony bromide modifications crystallize in the rhombic syngony and β – SbBr₃ is isostructural to trichloride (*table 3*). Elementary cells parameters α – and β – modifications are connected by the following ratios: 1/2 B_α ≈ a_β, 2c_α ≈ B_β, a_α ≈ c_β.

The molecular package in the structure β – SbBr₃ can be presented as a dense package of bromine atoms in slightly riffled layers parallel to plane (100). The layers are connected with each other by antimony atoms contained in the distorted octahedron voids [14]. ax /14/.

Table 3 – X-ray data for antimony (III) chloride and bromides

| | Chloride [12] | α – bromide [13] | β – bromide [14] |
|--|----------------------------------|---|----------------------------------|
| Syngony | rhombic | Rhombic | Rhombic |
| Space group | P bnm | P2 ₁ 2 ₁ 2 ₁ | P bnm |
| Cell parameters 10 ⁻¹ Nm | a = 6,37 b = 8,12 c = 9,47 | a = 10,12 b = 12,30 c = 4,42 | a = 6,68 b = 8,25 c = 9,96 |
| Number of form.units | 4 | 4 | 4 |
| ρ exp. g/cm ³ | | 4,35 | 4,27 |
| ρ calc. g/cm ³ | 3,09 | 4,37 | 4,38 |

The authors of [15] established the existence at high pressures of two more modifications both of antimony trichloride and tribromide, however in the work there was not discussed peculiarities of changing structures at these transformations. In work [15] there was carried out studying antimony trihalogenides and senarmonite by the method of nuclear gamma-resonance and stated that the chemical shift for ^{121}Sb is a linear function of electrical negation of halogen or oxygen atom.

Of chemical properties of antimony trichloride and tribromide there must be noticed their tendency to hydrolysis [17] with forming oxo-halogenides, which provides for a strong hygroscopicity of compounds.

THE SYSTEMS OF ANTIMONY (III) OXIDE

At the beginning of our studies there were no data about phase diagrams of antimony oxide-antimony chloride and antimony oxide-antimony bromide systems in publications. There were found only the data about the existence of antimony oxo-halogenides SbOCl [18-20], $\text{Sb}_4\text{O}_5\text{X}_2$ [11,22], $\text{Sb}_8\text{O}_{11}\text{X}_2$ [19] (where X= Cl, Br). The compounds were obtained by hydrolysis of a corresponding antimony trihalogenide at different starting solution concentrations and temperatures. For example, SbOX is formed at the ratio of antimony trihalogenide and water 1:8, $\text{Sb}_4\text{O}_5\text{X}_2$ 1:27 [20]. The composition of all the phases was established with the help of chemical analysis, their individuality was confirmed in all the cases except SbOBr and $\text{Sb}_8\text{O}_{11}\text{Br}_2$ X-ray graphically.

X-ray structural analysis was carried out for compounds SbOCl [18], $\text{Sb}_4\text{O}_5\text{Cl}_2$, $\text{Sb}_4\text{O}_5\text{Br}_2$ [18], $\text{Sb}_4\text{O}_5\text{Cl}_2$ [22]. Individual crystals necessary for the structural analysis in all the cases were obtained in hydrolysis. The results of the primary structural analysis are presented in table 4. By the data of work [18] the structure SbOCl consists of endless layers of $(\text{Sb}_6\text{O}_6\text{Cl}_4^{2+})_\infty$, connected by chlorine atoms, located between the layers, besides, interlayer chlorine atoms are in ion form. The crystal structure of isostructural $\text{Sb}_4\text{O}_5\text{Cl}_2$ and $\text{Sb}_4\text{O}_5\text{Br}_2$ are also characterized by the existence of endless antimony-and-oxygen layers $(\text{Sb}_4\text{O}_5^{2+})_\infty$ between them there are located halogen atoms [21, 22]. In the structure $\text{Sb}_4\text{O}_5\text{Cl}_2$ can be separated two different variants of coordination for antimony atoms: trigonal pyramid one of the equatorial apexes of which is taken by a free pair of electrons, and tetrahedron, one of the apexes of which is also taken by a free pair of electrons.

Crystal structure $\text{Sb}_8\text{O}_{11}\text{Cl}_2$ is not decoded but there is only established its belonging to triclinic syngony [19] (table 4).

The authors of works [21, 22] studied infrared spectra and spectra of combination scattering of compounds SbOCl , $\text{Sb}_4\text{O}_5\text{Cl}$ and $\text{Sb}_4\text{O}_5\text{Br}_2$ in frequency range 100-900 cm. Plate monocrystals (dimensions from 5 x 7 mm) were obtained for the phase $\text{Sb}_4\text{O}_5\text{Cl}$ by means of sublimation-condensation in vacuum ampoule at temperatures of evaporation and condensation 505 and

465°C, respectively. There was established semiconductor character of the compound, determined the forbidden zone width (3,77 eV) and specific resistance to electric current (3×10^9 Ohm x cm). Monocrystals are transparent in the range of 0,38-8 Mkm.

Table 4 – X-ray graphic data for antimony oxo-halogenides

| Phase Parameter | SbOCl /18/ | Sb ₄ O ₅ Cl ₂ /22/ | Sb ₄ O ₅ Br ₂ /21/ | Sb ₈ O ₁₁ Cl ₂ /19/ |
|---|--------------------|--|--|---|
| Syngony | Monoclin. | monoclin. | monoclin. | triclinial |
| Space group. | P2 ₁ /c | P2 ₁ /c | P2 ₁ /c | P $\bar{1}$ |
| Cell parameters 10 ⁻¹ Nm and degrees | a=9,54 | a=6,238 | a=6,61 | a=18,92 |
| | b=10,77 | b=5,111 | b=5,14 | b=4,03 |
| | c=7,94 | c=13,54 | c=13,47 | c=10,31 |
| | | | | α =88,0 |
| | β =103,6 | β =97,1 | β =97,7 | β =110,0 |
| | | | | γ =86,8 |
| z | 12 | 2 | 2 | 2 |
| ρ exp. g/cm ³ | 4,31 | 4,95 | 5,19 | 5,15 |
| ρ calc. g/cm ³ | 4,36 | 4,947 | 5,53 | 5,47 |

The temperature of congruent melting of phase Sb₄O₅Cl is $590 \pm 3^\circ\text{C}$. There were no data about obtaining monocrystals of other antimony oxo-chlorides and oxo-bromides in the publications. Thus, it can be considered proved that there exist only oxo-halogenides SbOCl, Sb₄O₅Cl, Sb₄O₅Br₂ and Sb₈O₁₁Cl₂. Absence of the X-ray phase analysis data doesn't permit to make a final conclusion as to existence of oxo-bromides SbOBr and Sb₈O₁₁Br₂.

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