

ON THE ORIGIN OF δ - Bi_2O_3 FORMATION AT LOW TEMPERATURES

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Abstract - The results of electron-diffraction studies of Bi_2O_3 films stable at low temperatures are shown in the present paper. A sufficiently detailed analysis of the formation of different phases in Bismuth Oxide thin layers has been carried out. The Bismuth films obtained by condensation in vacuum on NaCl cleavages and annealed in the air at 473 K are shown to correspond to a high-temperature cubic phase of δ - Bi_2O_3 with the parameter $a = 5.52 \pm 0.05 \text{ \AA}$. With increasing annealing temperature ($\sim 523 \text{ K}$) a transition to β -phase with the parameters $a = 10.95 \text{ \AA}$, $c = 5.631 \text{ \AA}$ takes place. On the base of the analysis of epitaxial relations of δ - and β -phases and the Bi ; attice as well as by estimation of reflection intensities, the formation of a high-temperature δ - Bi_2O_3 phase at a low temperature has been explained.

I. INTRODUCTION

In spite of rather great number of works dealing with investigation of Bismuth Oxide film growing regularities, the Bi-O system is still studied insufficiently. The structural data are available only on some Bi_2O_3 modifications without their stability region [1, 2], and relative to the other oxide of the system (BiO , Bi_2O_4 , Bi_2O_5) there is noted merely that they are still studied poorly.

Bi_2O_3 is the best studied oxide in the given system, but there is a number of contradictory data on this compound in literature. It has been already reported about the determination and refinement of Bi_2O_3 polymorph structure, and at present the four modifications of especially undoped and "pure" bismuth oxide denoted as α , β , γ and δ - Bi_2O_3 are distinguished. The results of studying the different stable and metastable phases of bismuth oxide are inconsistent

with respect to conditions of stable existence and phase transition, stoichiometry, space group definition, configuration and the unit cell sizes, and even relative to the existence of certain modifications.

The results of electron diffraction studies of the formation of δ - Bi_2O_3 films stable at low temperatures are shown in the present paper.

II. RESULTS AND DISCUSSION

The δ - Bi_2O_3 with the period $a = 5.50 - 5.60 \text{ \AA}$ obtained first by L.G.Sillen [3, 4] by melting of α - Bi_2O_3 samples for 2 hours in a chinaware crucible followed by a fast cooling is well-known. When studying this phase with the use of the paper patterns, he has found that its period is $a = 5.52 \pm 0.05 \text{ \AA}$. The X-ray powder patterns revealed only reflections with unmixed indices attributed to the scattering from the Bi atoms located in sites of the face-centered cubic (fcc) cell.

Later Gattow G. and Schroder H. [5] obtained the Bismuth Oxide modifications metastable at room temperature by melting Bi_2O_3 for 15 - 60 min together with the other oxides followed by a sharp cooling of the melt. They denoted the above modification as δ^* - Bi_2O_3 , determined its period, $a = 5.50 - 5.60 \text{ \AA}$, considering that the obtained δ^* - Bi_2O_3 and "a primitive cubic" Sillen modification is one and the same high-temperature phase of the bismuth oxide which can exist at room temperature being stabilized by oxygen ion impurities. When studying the structure using the X-ray powder patterns and the error method, it has been supposed that the δ^* - Bi_2O_3 crystallizes in CaF_2 structural type with a statistical oxygen atom distribution in the cell. Thus, both in Sillen and Gattow models the Bi atoms are located in the sites of the fcc cell, but the difference of

these models is in the location of the oxygen atoms and the appropriate choice of the space group.

A rather detailed analysis of the different phase formation in thin bismuth oxide films has firstly been carried out by Zavyalova A.A. and Imamov R.M. [6, 7, 8]. The analysis showed the possibility of obtaining the δ - Bi_2O_3 at low temperatures in particular.

Now, consider the problem of the origin of the formation of δ - Bi_2O_3 and β - Bi_2O_3 high-temperature modifications in thin Bi_2O_3 films at room temperature (or somewhat higher, ~ 473 K) in more detail. As seen from the Bi-O state diagram (Fig.1), the above modifications are stable at temperature above 873 K [9, 10].

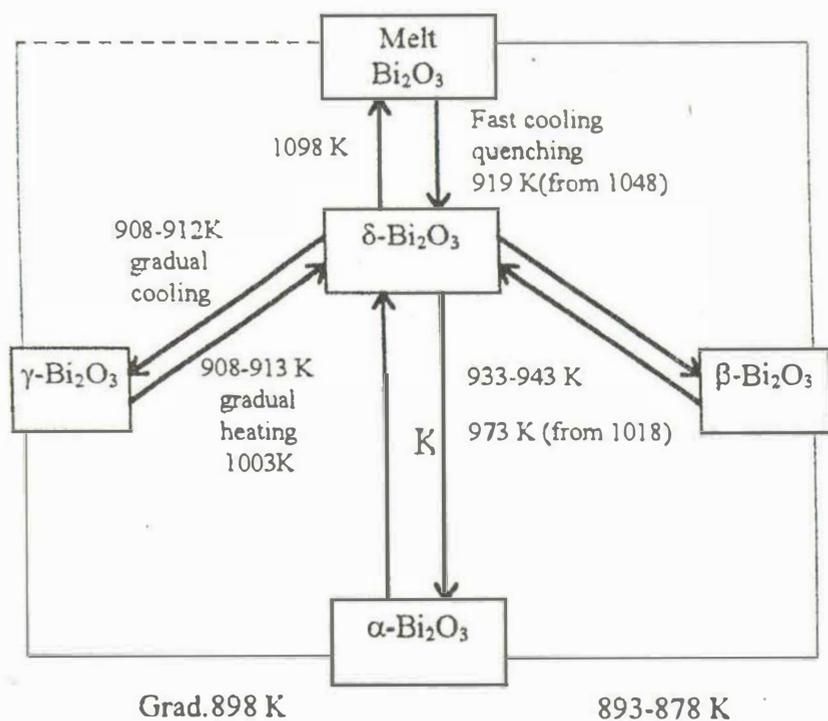


Fig.1 Polymorphous Transitions for "Pure" Bismuth Oxides.

The electron diffraction is known to reveal the light atoms much better than the X-ray diffraction. Therefore the studies of the obtained electron diffraction patterns allow to judge more correctly which of the models is a reliable one, i.e. corresponds to the intensity distribution observed on electron diffraction patterns.

Electron diffraction studies showed that in our case the δ - Bi_2O_3 is the main oxidation product. Moreover, in electron diffraction patterns of bismuth films obtained by condensation in vacuum on NaCl cleavages and annealed in the air at 473 K (Fig.2) one can observe the rings corresponding to the δ - Bi_2O_3 cubic lattice with the parameter $a = 5.52 \pm 0.05 \text{ \AA}$ typical of the high-temperature phase of δ - Bi_2O_3 . As the annealing temperature increases (~ 523 K), the strengthening of the lines takes place at first and then the lines corresponding to β - Bi_2O_3 with the parameters $a = 10.952 \text{ \AA}$, $c = 5.631 \text{ \AA}$ occur (Fig.3). This is probably due to the fact that the δ - and β - phases of Bi_2O_3 are closely connected to each other. Their difference is in a statistical location of the oxygen vacancies in the δ - Bi_2O_3 structure because in this case 6 oxygen atoms

occupy the 8-fold position. A partial ordering of these atoms takes place even in a cubic δ -phase. The ordering of two vacancies per cell in the oxygen sublattice of δ - Bi_2O_3 leads to the formation of β - Bi_2O_3 with a lattice parameter increased almost by a factor of two. Therefore the β - Bi_2O_3 is somewhat a superstructure of the δ - Bi_2O_3 cubic oxide.

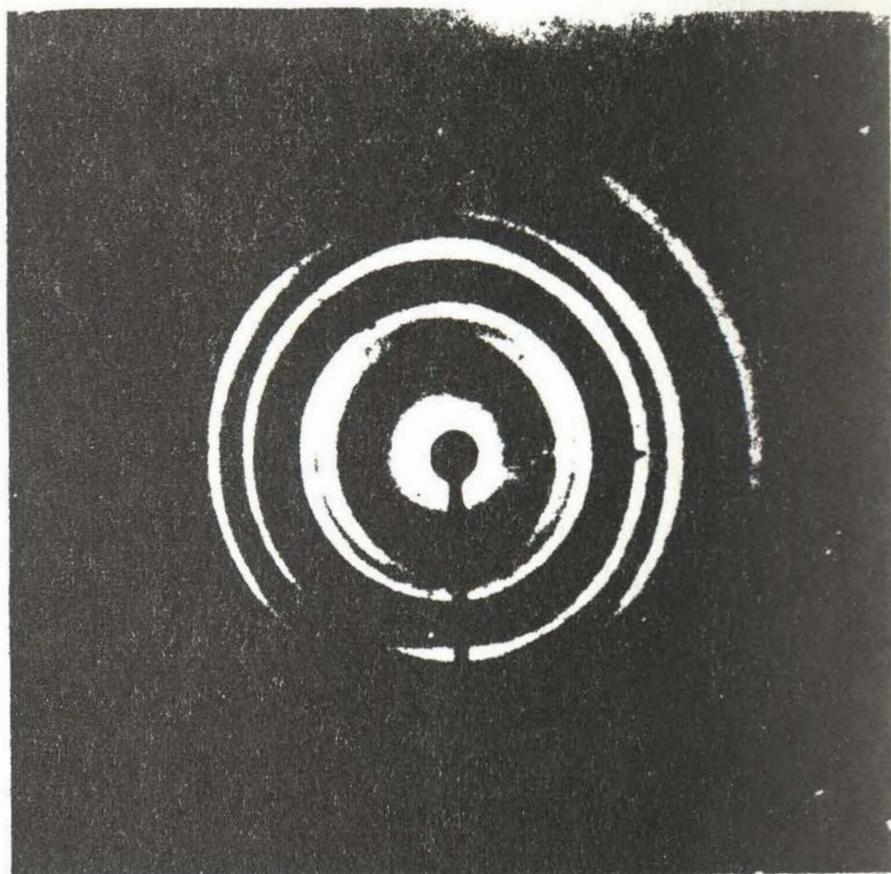


Fig.2 Transmission Electron Diffraction Pattern of δ - Bi_2O_3 on NaCl : Annealed in the Air at Temperature of 473 K for 10 Hours.

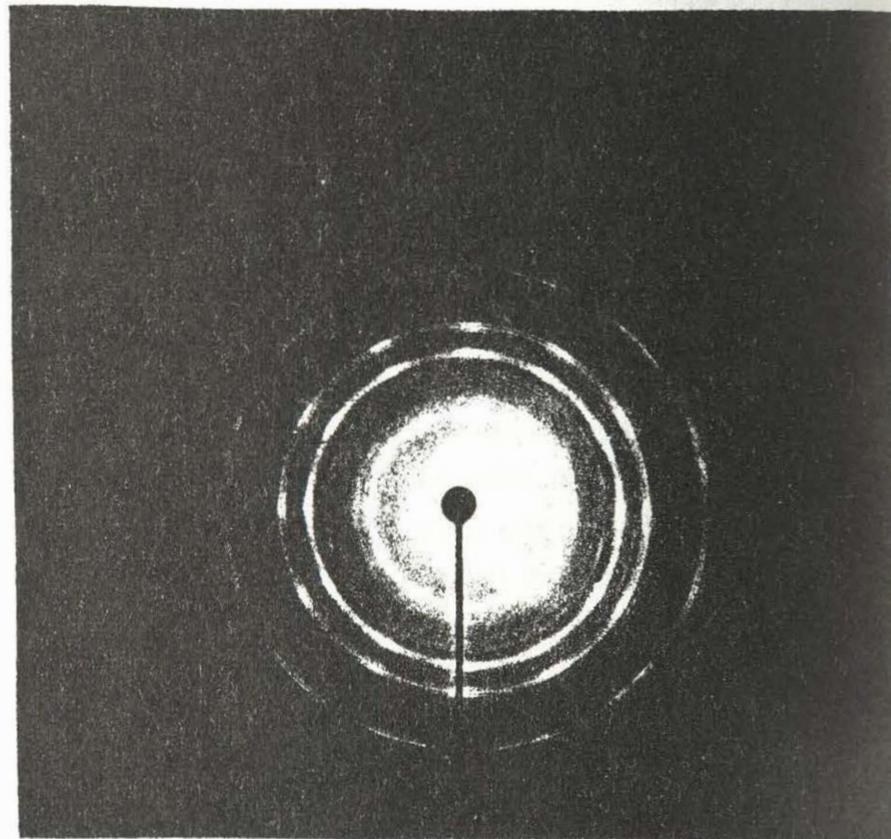


Fig.3 Transmission Electron Diffraction Pattern of $(\delta + \beta)$ -Phases of Bi_2O_3 on NaCl : Annealed in the Air at $T = 523$ K for 10 Hours.

The analysis of the epitaxial relations between the δ - and β -phases lattice parameters and the Bi lattice has shown that the diffusion of oxygen atoms into the bismuth lattice is observed during the oxidation process. The results of the above analysis coincide with the data of [12]. This corresponds to an overall regularity of metal oxidation. The oxide is formed in such a modification and is oriented on metal so that the rearrangement of a metal lattice to the lattice of its oxide takes place at a minimal shift of metal ions. This fact, to our opinion, is the main reason of the formation of the δ - and β -phases of Bi_2O_3 during the oxidation of bismuth at temperature below the melting temperature.

When investigated the point electron diffraction patterns of Bi_2O_3 it was found that besides the reflections (hkO), sometimes a very weak net of virtual reflections is observed on the electron diffraction patterns. Primarily we have taken them as the reflections (hk1) assuming that the electron diffraction patterns of such a type are a mixture of two orientations by (001) and (011) planes parallel to the face of the NaCl cube. But the above diffraction patterns can also be taken as a plane (hkO) of a cubic cell with a period $a = 5.45 \text{ \AA}$ [6]. The latter is more probable as the far reflections are displayed better on the base of the cell with $a = 5.45 \text{ \AA}$. Therefore, we considered such patterns as the sections of the reciprocal lattice of the cubic crystals over the planes (hkO) (Fig.4).

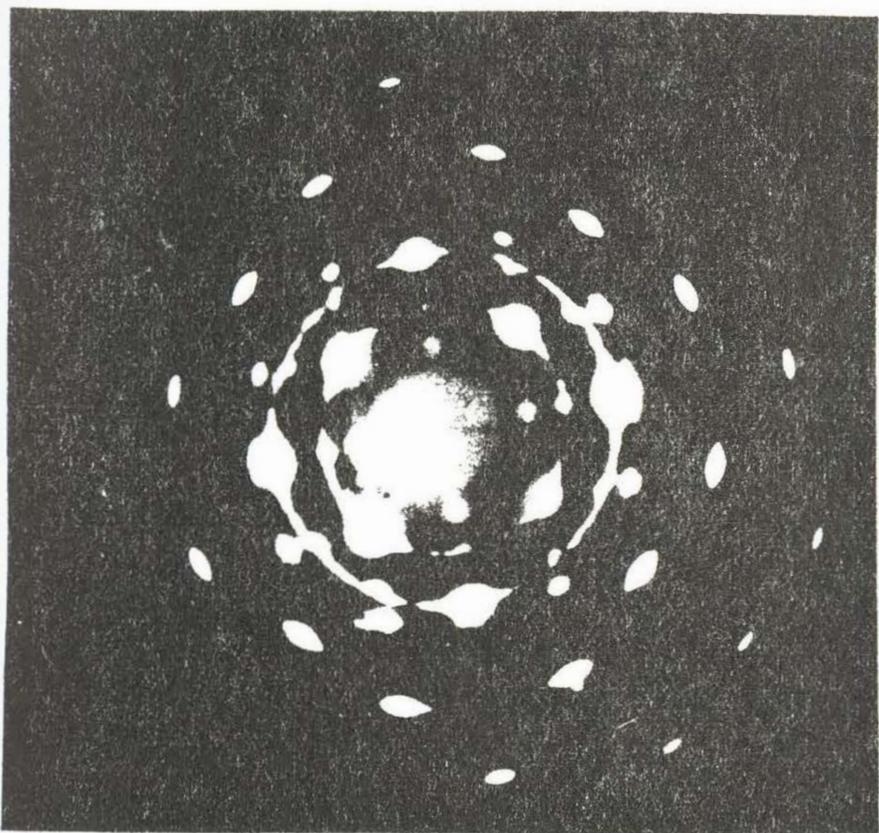


Fig.4 Transmission Electron Diffraction Pattern of δ - Bi_2O_3 Films on NaCl ; Annealed in The Air at $T = 573 \text{ K}$ for 10 Hours.

When studied the structure of powder pattern by the error method, Sillen [3] concluded that the atoms occupy the following point positions in the Fedorov's group : Pn3m

4 Bi	4 (c)
6 O	6 (d)

There are 4 Bi atoms per unit cell. The coordination number of Bi is six, coordination polyhedron is a cube where the six vertices of 8 are occupied. The coordination number of oxygen is 4, the coordination polyhedron is a tetrahedron. The distances of Bi - O and O - O are 2.40 \AA and 2.76 \AA , respectively. Sillen called this modification of bismuth oxide as "primitive cubic".

Later Gattow and Schroder [5] obtained a metastable phase of the Bi oxide melting Bi_2O_3 together with As_2O_3 , Sb_2O_3 , Nb_2O_5 , TaO_5 , WO_3 , SnO_2 , SiO_2 , TiO_2 and cooling them sharply. They denoted the above metastable phase as δ^* - Bi_2O_3 with a period $a = 5.50 - 5.60 \text{ \AA}$ (depending on the impurity ion).

The authors [5] consider that the obtained δ^* - Bi_2O_3 and "a primitive cubic" Sillen modification is one and the same high-temperature phase of the bismuth oxide which can exist at room temperature being stabilized by impurities of foreign ions (it probably is Si by Sillen as Bi_2O_3 has been melted in a china crucible).

Gattow and Schroder studied the structure with powder patterns by the error method and unlike Sillen they proposed a following structure model in the space group Fm3m :

4 Bi	4 (a)
6 O	8 (c)

i.e. δ^* - Bi_2O_3 crystallizes in a CaF_2 structural type with a statistical distribution of six oxygen atoms in the cell. The distances of Bi-O and O - O are 2.45 \AA and 2.83 \AA , respectively. It is seen that in Sillen and Gattow models the Bi atoms are located over the sites of the fcc cell, and they differ from one another by the position of oxygen atoms and by the space group. It should be noted that Sillen does not explain why the space group $O_h^4(\text{Pn}3\text{m})$ was namely chosen [3]. Gattow and Schroder, unlike Sillen, consider all the possible space groups in detail and do not take into account all of them, except for Pn3m and Fm3m, as highly improbable. The above groups are essentially different due to a lack of sixfold point positions in the $O_h^5(\text{Fm}3\text{m})$ group and hence, the oxygen atoms should be located statistically. Comparing the calculated and the picnometric densities for Sillen model in the space group Pn3m with those for the space group (Fm3m) of their proposed model, Gattow and Schroder concluded that Sillen was wrong and the obtained high-temperature modification of the bismuth oxide crystallizes in a CaF_2 structural type.

The both works were made with the help of powder patterns. But the latter gives the information only about the position of bismuth atoms. Therefore the oxygen atom location and hence the space group were chosen only from the crystallochemical point of view.

The electron diffraction reveals the light atoms considerably better as compared to the X-ray diffraction. Therefore, our point electron diffraction patterns, unusable due to insufficiently good quality for a complete structural determination, allow to judge which of the models proposed is valid, i.e. corresponds to the intensity distribution observed on electron diffraction patterns.

The electron diffraction pattern (Fig.4) is a section of the reciprocal lattice of a cubic crystal over the (hk0) planes. In this case, the reflections with $h + k = 2n$ are observed. As seen from Table 1, where the reflection intensities estimated qualitatively are listed, all the reflections with even h and k are strong, and they are weak with odd h and k . In other words, a strong net of reflections forming a fcc lattice as well as a weak net of reflections with the mixed indices are observed on electron diffraction patterns. But Gattow and Schroder did not observe the weak reflections with mixed indices, and therefore they considered a cell to be a face centered cubic one. For this reason, their model cannot be taken into account. A weakness of the mixed reflections indicates that they are attributed to the scattering only from the oxygen atoms. This fact entirely agrees with Sillen model (in Pn3m). Really, for this model $\Phi_{th}^{hk0} = 4f_e^{Bi} + 6f_e^o$ and $\Phi_{th}^{hk0} = 2f_e^o$ for reflections with even and odd h and k , respectively.

Table I

The Calculation of Electron-Diffraction Pattern of The Phase With bcc Lattice of δ -Bi₂O₃ Films Obtained on NaCl and Annealed at 570 K for 10 h, $2\ell\lambda = 53.56$ mm Å

No	2 (mm)	d_{exp} (Å)	Intensity	hkl	a (Å)
1	13.6	3.938	weak	110	5.513
2	19.4	2.760	high	200	5.520
3	27.4	1.954	high	220	5.525
4	30.6	1.754	weak	310	5.533
5	38.8	1.380	high	400	5.520
6	43.2	1.239	high	420	5.540
7	58	0.920	high	600	5.520
8	59	0.907	weak	610	5.517
9	61.2	0.873	high	620	5.521
10	65	0.824	weak	630	5.527

$$a_{aver.} = 5.5236 \text{ (Å)}$$

Thus, the intensity distribution observed on electron diffraction patterns confirms the structure model proposed by Sillen [3]. In this case it should be noted that in spite of the fact that the Bi₂O₃ structure is described by the Fedorov's group Pn3m, its unit cell is not a primitive cubic cell (by Sillen) but it is a bcc cell as the bismuth and the oxygen atoms occupy the particular positions satisfying the condition $h + k + \ell =$

$2n$. As for the structure determined by Gattow and Schroder, if the δ -Bi₂O₃ modification is the same Bi₂O₃ modification obtained by Sillen and observed by us (as the authors consider themselves and is the most probable as the structure remains unchanged when introducing different impurity ions), then the model proposed is probably not valid. Moreover, the factor $R = 0.019$ given in [5] seems to be too "good" to be reliable.

III. CONCLUSION

It should be noted that the obtained results are in a good agreement with the data of L.S.Palatnik et al. [11, 12]. Both in our work and in experiments carried out by L.S.Palatnik et al. the bismuth oxide films were undoped intentionally. The mass spectral studies of films did not reveal a considerable amount of alkaline metal ions which could diffuse from a substrate. Nevertheless, in our case, as in L.S.Palatnik's works, the films of high-temperature δ - and β -Bi₂O₃ phases have been observed, while a monoclinic α -phase stable at room temperature has not been revealed. It is probably due to the fact that a radical change of interatomic bonds and the large shifts of Bi atoms, i.e. great energy consumption which cannot be provided at low temperatures, is necessary for the rearrangement of the Bi lattice to a monoclinic α -phase lattice stable at low temperatures. The formation of Bi₂O₃ is possible during the oxidation of liquid bismuth when the Bi lattice disappears (destroys) and does not impose any restrictions on the structure of the oxide formed.

We consider that the stability of the obtained high-temperature δ -Bi₂O₃ phase can be attributed to the uncontrolled impurities of foreign ions. The concentration of such ions can be rather high. Therefore, due to the difference of ionic radii, they can from the large macrostresses in lattice which are capable of stabilization of high-temperature phases at low temperatures.

REFERENCES

- [1] A.E. Vol, "Stroenie i Svoistva Dvoinykh Metallicheskih Sistem", Fizmatgiz, v.2, p.982 Moscow, 1962.
- [2] I.Narei-Sabo, "Neorganicheskaya Kkristalloghimiya", Izd., p.504, An Hungary, 1969.
- [3] L.G. Sillen, "X-ray Studies on Bismuth Trioxide", Ark. Kemi. Mineral. Geol., v.12 A, n.18, p.1-15, 1937.
- [4] L.G. Sillen, "Crystal Structure of Monoclinic α -Bi₂O₃", Z. Kristallogr., v.103, p.274-290, 1941.

- [5] G. Gattow, H. Schroder, "Die Kristallstruktur Der Hechtemperatur Modifikation Von Wismut (111)-oxid δ - Bi_2O_3 ", Z. Allgem. Chem., bd.318, n.3-4, p.176-189, 1962.
- [6] A.A. Zavyalova, R.M. Imamov, "K Voprosu o Kubicheskoi Strukture δ - Bi_2O_3 ", Kristallografiya, n.2, v.14, p.331-333, 1969.
- [7] A.A. Zavyalova, R.M. Imamov, "K Voprosu o Strukture β - $\text{Bi}_2\text{O}_{2.5}$ v Tonkikh Sloyakh", Kristallografiya, n.3, v.16, p.516-519, 1971.
- [8] A.A. Zavyalova, R.M. Imamov, Z.G. Pinsker, "Elektronnograficheskoe Issledovanie Sistemy Bi-O o Tonkikh Sloyakh", Kristallografiya, n.4, v.10, p.480-482, 1965.
- [9] L.D. Fomchenkov, A.A. Mayer, N.A. Gracheva, "Polimorfizm Okisi Vismuta", Neorg. Mater. n.11, v.10, p.2020-2023, 1974.
- [10] C.Wang, X.Xu, B.Li, "Ionic and Electronic Conduction of Oxygen Ion Conductors in the Bi_2O_3 System", Solid State Ionics., v.13, p.135-140, 1984.
- [11] L.S. Palatnik, A.I. Fedorenko, B.A. Savitski, V.I. Korobko, "Izuchenie Khimicheskikh i Strukturnykh Prevrashenii, Sopotstvuyushikh Spitaksialnomu Rostu Vismuta na Shelochnogaloidnykh ristallakh", Fiz. Tverd. Tela. N.8, v.16, p.2291-2291, 1974
- [12] L.S. Palatnik, A.I. Fedorenko, B.A. Savitski, "Fazoyava Neravnovesnost pri Okislenii Plenok Vismuta", Ser. Fizika, n.11, v.38, p.2377-2381, Izv.An SSSR, 1974.

