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CRYSTAL STRUCTURE OF THE COMPOUND $BI_{3.43}RE_{0.57}O_{6.29}$

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The work investigates the crystal structure of a non-stoichiometric oxide compound of the composition $Bi_{3.43}Re_{0.57}O_{6.29}$*, belonging to the* Bi_2O_3*–*Re_2O_7 *system, which attracts considerable attention due to its high oxide-ionic conductivity and prospects for use in solid-state electrochemistry. The relevance of the study is due to the need to search for new materials with improved transport properties, in particular for use in solid oxide fuel cells and oxygen sensors. The aim of the work is to establish the features of the crystal structure, cation ordering and state of the oxygen sublattice of the studied compound. To achieve this goal, the X-ray powder diffraction method was used with subsequent refinement of the structure by the Rietveld method. The samples were obtained by melting the starting oxides with subsequent quenching, which ensured the formation of a single-phase material. As a result of the study, it was established that the compound* $Bi_{3.43}Re_{0.57}O_{6.29}$ *crystallizes in the structural type* δ*-*Bi_2O_3 *with cubic symmetry and space group* $Fm\bar{3}m$*. The unit cell parameter* $a = 5.7363(1)$ *Å was determined. It was shown that Bi and Re atoms statistically occupy one crystallographic position, which indicates their partial mutual substitution in the cation sublattice. It was established that the oxygen sublattice is characterized by partial filling of positions, which indicates the presence of a significant number of oxygen vacancies. These vacancies play a key role in the formation of high oxide-ionic conductivity, creating effective migration paths for oxygen ions. The non-stoichiometric composition contributes to additional structural defects and stabilization of the high-temperature* δ*-phase at room conditions. The obtained results are consistent with the literature data and confirm that the studied compound belongs to the class of defective fluorite-like oxides. The revealed structural features, in particular the disorder of the oxygen sublattice and the statistical distribution of cations, determine the prospects of the material as an effective oxide-ionic conductor. The work expands the understanding of the mechanisms of defect structure formation in oxides of the Bi–Re–O system and can be used for further targeted synthesis of new functional materials.*

Key words: *X-ray structural analysis, crystal structure, Rietveld method.*

Заводянний В. В. Кристалічна структура сполуки $Bi_{3.43}Re_{0.57}O_{6.29}$

У роботі досліджено кристалічну структуру нестехіометричної оксидної сполуки складу $Bi_{3.43}Re_{0.57}O_{6.29}$*, що належить до системи* Bi_2O_3*–*Re_2O_7*, яка привертає значну увагу завдяки високій оксид-іонній провідності та перспективам використання у твердотільній електрохімії. Актуальність дослідження зумовлена необхідністю пошуку нових матеріалів із покращеними транспортними властивостями, зокрема для застосування у твердоксидних паливних елементах та сенсорах кисню.*

Метою роботи є встановлення особливостей кристалічної структури, катіонного впорядкування та стану кисневої підґратки досліджуваної сполуки. Для досягнення поставленої мети застосовано метод рентгенівської порошкової дифракції з подальшим уточненням структури методом Рітвельда. Зразки отримували шляхом плавлення вихідних оксидів із подальшим гартуванням, що забезпечило формування однофазного матеріалу.

У результаті дослідження встановлено, що сполука $Bi_{3.43}Re_{0.57}O_{6.29}$ *кристалізується у структурному типі* δ*-*Bi_2O_3 *з кубічною симетрією та просторовою групою* $Fm\bar{3}m$*. Визначено параметр елементарної комірки* $a = 5.7363(1)$ *Å. Показано, що атоми Bi і Re* *статистично займають одну кристалографічну позицію, що свідчить про їх часткове взаємне заміщення у катіонній підґратці.*

Встановлено, що киснева підґратка характеризується частковим заповненням позицій, що вказує на наявність значної кількості кисневих вакансій. Саме ці вакансії відіграють ключову роль у формуванні високої оксид-іонної провідності, створюючи ефективні шляхи міграції іонів кисню. Нестехіометричний склад сприяє додатковій дефектності структури та стабілізації високотемпературної δ-фази при кімнатних умовах.

Отримані результати узгоджуються з літературними даними та підтверджують, що досліджувана сполука належить до класу дефектних флюоритоподібних оксидів. Виявлені структурні особливості, зокрема розупорядкованість кисневої підґратки та статистичний розподіл катіонів, визначають перспективність матеріалу як ефективного оксид-іонного провідника. Робота розширює уявлення про механізми формування дефектної структури в оксидах системи Bi–Re–O та може бути використана для подальшого цілеспрямованого синтезу нових функціональних матеріалів.

Ключові слова: *рентгеноструктурний аналіз, кристалічна структура, метод Рітвельда.*

Introduction. Complex oxide materials based on bismuth occupy an important place among functional inorganic compounds due to their high oxide-ionic conductivity, significant defectivity of the crystal structure, and the ability to stabilize high-temperature phases at room temperature [1–3]. Of particular interest is the δ-modification of Bi_2O_3, which is characterized by a fluorite-like crystal structure with a high concentration of oxygen vacancies. It is the presence of a large number of vacancies in the oxygen sublattice that provides extremely high values of oxide-ionic conductivity, which significantly exceed the indicators of most known solid electrolytes [1, 3]. It is known that stabilization of δ-Bi_2O_3 is possible by doping with high-valence cations, in particular transition metals [2, 3]. As a result of such doping, complex oxide systems with a structure related to fluorite are formed. Among such systems, the Bi_2O_3–Re_2O_7 system is of considerable interest. In the Bi-enriched region of this system, a series of oxides of the composition $Bi_{2-x}Re_xO_{3+2x}$ is formed, which are characterized by a defective fluorite-like structure [4, 5]. The structural features of these compounds are determined by the complex interaction between cation ordering and the distribution of oxygen vacancies. The thermal evolution and structural properties of the δ-Bi_2O_3-related compound Bi_9ReO_{17} were studied using neutron and synchrotron powder diffraction, as well as electron diffraction [6]. It was found that this phase is stable up to a temperature of about 725 °C, after which a transition occurs to a disordered phase similar to δ-Bi_2O_3, which is described by a cubic structure of the $Fm\bar{3}m$ type with a lattice parameter a = 5.7809(1) Å [6]. In [7], a combined experimental and computational study of the oxide-ionic conductor $Bi_{28}Re_2O_{49}$ was carried out, which allowed us to establish the mechanisms of oxygen ion migration in this material. It was shown that the variable coordination of rhenium atoms plays a key role in the formation of ionic conductivity mechanisms. The interaction between the Bi–O and Re–O sublattices ensures the formation of additional O^{2-} vacancies and forms effective diffusion paths for oxygen ions. Despite a significant number of studies of phase relations in the Bi_2O_3–Re_2O_7 system, the structural features of non-stoichiometric compounds with a composition different from the stoichiometric phases remain insufficiently studied [4–7]. The search for new functional oxide materials with high oxide-ionic conductivity is an important direction in modern materials science and solid-state chemistry. Such materials can be used as electrolytes in solid oxide fuel cells, oxygen sensors and other electrochemical devices [1, 2]. Establishing the regularities of the formation of a defect structure in complex oxides of the Bi–Re–O system is necessary for understanding the mechanisms of ionic conductivity and developing new functional materials. In this context, the study of a non-stoichiometric compound of the composition $Bi_{3.43}Re_{0.57}O_{6.29}$ is relevant, since it allows establishing the relationship between the cation ratio, the features of atomic ordering and the formation of a defective oxygen sublattice, which directly affects the physicochemical properties of the material [5–7]. The aim of the work is to establish the crystal structure of a non-stoichiometric compound of the composition $Bi_{3.43}Re_{0.57}O_{6.29}$, as well as to determine the features of atomic ordering and the defective oxygen subsystem.

Presentation of the main material. To achieve the goal, it is necessary to solve the following tasks: Generate the diffraction spectrum of the studied compound using the ICDD PDF-2 (2004) database under card number 00-043-0195 Determine the phase composition of the synthesized sample by X-ray powder diffraction. Establish the parameters of the unit cell of the studied phase. Carry out indexing of the compound. Refine the crystal structure by the Rietveld method [8]. Analyze the distribution of Bi and Re cations in the crystal lattice. Investigate the features of the arrangement of oxygen atoms and the possible presence of oxygen vacancies. Assess the influence of non-stoichiometry on the structural stability of the obtained phase. Methods. Samples for studying the diffraction spectrum were obtained by melting a mixture of Bi_2O_3 and ReO_2 at 920 °C for 3 minutes with subsequent quenching in ice water. [9]. The powder diffraction spectrum was recorded on a copper filtered radiation (λ=1.54060A0) with Bragg-Brentano imaging geometry [9]. The obtained diffraction spectrum was analyzed based on literature data using the HighScore 3.0 program and the attached pdf-2 database for 2004. The δ-Bi2O3 structure type was chosen as the basis for studying the crystal structure of the compound $Bi_{3.43}Re_{0.57}O_{6.29}$ [10]. As a result of refining the crystal lattice parameters by the Rietveld method [9], it was established that the compound belongs to the δ-Bi2O3 structural type [10] with the microstructural parameters given in Table 1, has a cubic lattice and belongs to the space group Fm3 ˉm (225) with lattice periods a=5.7363(1).

Table 1

Microstructural parameters of the crystal structure
of the compound $Bi_{3,43}Re_{0,57}O_{6,29}$

Atom	Wyck.	s.o.f.	*x*	*y*	*z*
Bi	4a	0,857500	0	0	0
Re	4a	0,142500	0	0	0
O	32f	0,786250	0,924(1)	0,924(1)	0,924(1)

The calculated crystal structure data are given in Table 2.

The divergence factor R=4.05%. The obtained results of X-ray structural analysis indicate that the synthesized compound of the composition $Bi_{3.43}Re_{0.57}O_{6.29}$ crystallizes in the structural type δ-Bi_2O_3 with cubic symmetry and space group $Fm\bar{3}m$. The unit cell parameter a = 5.7363(1) Å agrees well with the literature data for oxides of the Bi–Re–O system, which have a defective fluorite-like structure.

It was established that Bi and Re atoms statistically occupy the crystallographic position 4a, which is typical for δ-Bi_2O_3-like structures. Partial replacement of Bi^{3+} by Re cations leads to a redistribution of the electron density in the cation sublattice and contributes to the stabilization of the high-temperature δ-phase at room temperature. A similar stabilization mechanism is observed for other doped modifications of Bi_2O_3. The oxygen sublattice plays a special role in the formation of the structure. According to the refined structural parameters, oxygen atoms occupy the 32f position with partial filling (s.o.f. = 0.786250), which indicates the presence of a significant number of oxygen vacancies. It is such vacancies that are a characteristic feature of defective fluorite-like structures and determine their high oxide-ionic conductivity. Comparison of the calculated and experimental values of interplanar distances and diffraction angles shows their good agreement. Small deviations between 2θcal and 2θobs do not exceed the limits of experimental error, which confirms the correctness of the indexing and the adequacy of the proposed structural model. The value of the discrepancy factor R = 4.05% indicates a high quality of the structure refinement by the Rietveld method. The non-stoichiometric composition of the studied compound causes the appearance of additional structural defects, which can affect the stability of the crystal lattice and the transport properties of the material. The inclusion of Re atoms in the cationic sublattice changes the local coordination environment of oxygen and promotes the formation of a branched network of oxide-ion migration pathways. This is consistent with the literature data on the increased ionic conductivity in bismuth-rhenium oxides. Thus, the obtained results confirm that the compound $Bi_{3.43}Re_{0.57}O_{6.29}$ is a representative of defective fluorite-like oxides, which are characterized by significant structural disorder of the oxygen sublattice and a high concentration of vacancies. It is these features that can ensure the prospects of the studied material as a potential oxide-ionic conductor. In this structure, the Bi and Re atoms occupy the same crystallographic site (partial replacement), therefore: • they have the same local environment • accordingly, form the same type of coordination polyhedron In the image, this is shown as two separate, but geometrically identical polyhedra: BiO_8 and ReO_8

Table 2

Calculated values (2θ angle, interplanar distances and relative intensities) and given in ICDD for the compound $Bi_{3,43}Re_{0,57}O_{6,29}$.

	$2\theta_{cal}$	$2\theta_{obc}$	d_{cal}	d_{obs}	I_{cal}	I_{obs}	H	K	L
1	26,8925	26,890	3,31264	3,31300	100	100	1	1	1
2	31,1519	31,160	2,86874	2,86800	45,42	36	2	0	0
3	44,6380	44,647	2,02837	2,02800	25,71	27	2	2	0
4	52,8879	52,880	1,72976	1,73000	24,92	23	3	1	1
5	55,4368	55,441	1,65611	1,65600	7,68	5	2	2	2
6	64,9718	64,982	1,43420	1,43400	2,21	2	4	0	0
7	71,6468	71,653	1,31610	1,31600	8,85	4	3	3	1
8	73,8108	73,796	1,28277	1,28300	6,48	3	4	2	0
9	82,274	82,250	1,1709	1,17120	5,92	2	4	2	2
10	88,496	88,491	1,1040	1,10400	5,4	1	5	1	1
11	105,205	105,176	0,9696	0,96980	2,42	1	5	3	1
12	107,358	107,350	0,9560	0,95610	4,98	1	4	4	2

Each central atom (Bi or Re) is surrounded by eight oxygen (O) atoms (coordination number 8). The polyhedron is a distorted orthogonal (eight-coordination) polyhedron. It is not a perfect cube or square antiprism, but a deformed 8-vertex polyhedron. The reasons for the distortion are different bond lengths Bi–O / Re–O, features of the crystal lattice and mixed population of Bi/Re sites. The central atom can be Bi or Re, oxygen atoms form the vertices of the polyhedron. Edges are drawn between oxygen atoms and form a closed geometric structure. A common Bi/Re site means statistical substitution, i.e. there are bismuth or rhenium atoms. Oxygen atoms connect the polyhedra to each other. BiO_8 / ReO_8 polyhedra are the basic building blocks of the structure, their connection determines: packing density, electronic properties, ionic conductivity

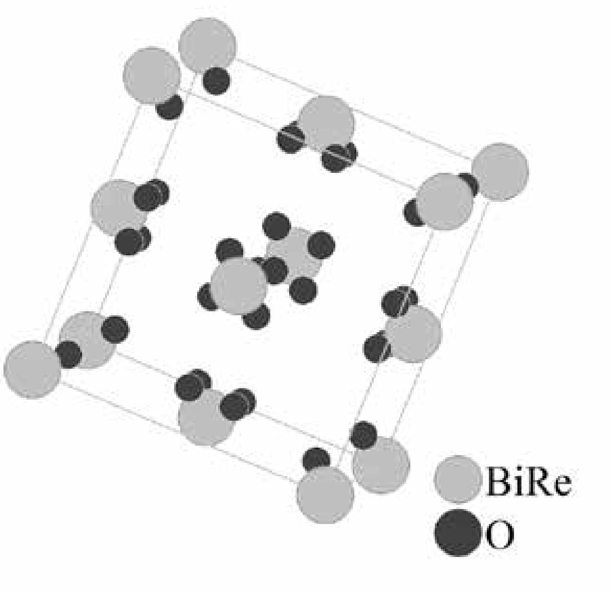

Fig. 1. Image of the crystal structure of the compound $Bi_{3.43}Re_{0.57}O_{6.29}$

Fig. 2. Coordination polyhedra for $Bi_{3.43}Re_{0.57}O_{6.29}$
(central site Bi/Re with cubic O8 coordination)

Conclusions and prospects for further research.

1. The crystal structure of the non-stoichiometric compound $Bi_{3.43}Re_{0.57}O_{6.29}$ was studied by X-ray powder diffraction.

2. It was established that the studied compound crystallizes in the structural type δ-Bi_2O_3 with cubic symmetry and space group $Fm\bar{3}m$ (№ 225).

3. As a result of the refinement of the structure by the Rietveld method, the unit cell parameter a = 5.7363(1) Å, as well as the position of atoms in the crystal lattice, were determined.

4. It is shown that Bi and Re atoms are statistically distributed in the 4a position, while oxygen atoms occupy the 32f position with partial filling, which indicates the presence of a significant number of oxygen vacancies.

5. The presence of vacancies in the oxygen sublattice and partial replacement of bismuth cations by rhenium atoms stabilize the defective fluorite-like structure and can contribute to the formation of effective migration paths for oxide ions.

6. The obtained results expand the understanding of the structural features of non-stoichiometric oxides of the Bi_2O_3–Re_2O_7 system and can be used in the further search for new materials with high oxide-ionic conductivity.

BIBLIOGRAPHY:

1. Sammes N. M., Tompsett G. A., Näfe H., Aldinger F. Bismuth based oxide electrolytes – structure and ionic conductivity *Journal of the European Ceramic Society*. 1999. Vol. 19, No. 10. P. 1801–1826. https://doi.org/10.1016/S0955-2219(99)00009-6.

2. Kharton V. V., Marques F. M. B., Atkinson A. Transport properties of solid oxide electrolyte ceramics: a brief review *Solid State Ionics*. 2004. Vol. 174, No. 1–4. P. 135–149. https://doi.org/10.1016/j.ssi.2004.06.015.

3. P. Shuk, H. Wiemhöfer, U. Guth, W. Göpel, M. Greenblatt. Oxide ion conducting solid electrolytes based on Bi_2O_3 *Solid State Ionics*. 1996. Vol. 89, No. 3–4. P. 179-196. https://doi.org/10.1016/0167-2738(96)00348-7.

4. Sleight A. W., Gillson J. L., Weiher J. F. Crystal structures and properties of bismuth rhenium oxides *Inorganic Chemistry*. 1974. Vol. 13, No. 3. P. 617–626. https://doi.org/10.1021/ic50133a023.

5. T. Fries G. Lang, S. Kemmler-Sack Defect fluorite structures in the Bi-rich part of the system Bi_2O_3 Re_2O_7 *Solid State Ionics* Volume 89, Issues 3-4,2 August 1996, Pages 233-240 https://doi.org/10.1016/0167-2738(96)00272-X

6. Neeraj Sharma, Ray L. Withers, Kevin S. Knight, Chris D. Ling Structure, crystal chemistry and thermal evolution of the δ-Bi_2O_3-related phase Bi_9ReO_{17} *Journal of Solid State Chemistry* Volume 182, Issue 9, September 2009, Pages 2468-2474 https://doi.org/10.1016/j.jssc.2009.07.008

7. Mark R. Johnson, Ivana Radosavljević Evans The mechanism of oxide ion conductivity in bismuth rhenium oxide, $Bi_{28}Re_2O_{49}$ *Solid State Ionics* Volume 244, 1 August 2013, Pages 35-39 https://doi.org/10.1016/j.ssi.2013.05.004

8. Rietveld H. M. A profile refinement method for nuclear and magnetic structures *Journal of Applied Crystallography*. 1969. Vol. 2, No. 2. P. 65–71. https://doi.org/10.1107/S0021889869006558.

9. Database PDF-2 від International Centre for Diffraction Data https://www.icdd.com

10. Dr. H. A. Harwig On the Structure of Bismuthsesquioxide: The α, β, γ, and δ-phas *Zeitschrift für anorganische und allgemeine Chemie 1978 Vol.444 p.151-166.* https://doi.org/10.1002/zaac.19784440118

REFERENCES:

1. Sammes N. M., Tompsett G. A., Näfe H., Aldinger F. (1999) Bismuth based oxide electrolytes – structure and ionic conductivity *Journal of the European Ceramic Society*. Vol. 19, No. 10. P. 1801–1826. https://doi.org/10.1016/S0955-2219(99)00009-6.

2. Kharton V. V., Marques F. M. B., Atkinson A. (2004) Transport properties of solid oxide electrolyte ceramics: a brief review *Solid State Ionics*. Vol. 174, No. 1–4. P. 135–149. https://doi.org/10.1016/j.ssi.2004.06.015.

3. P. Shuk, H. Wiemhöfer, U. Guth, W. Göpel, M. Greenblatt. (1996) Oxide ion conducting solid electrolytes based on Bi_2O_3 *Solid State Ionics*. Vol. 89, No. 3–4. P. 179-196. https://doi.org/10.1016/0167-2738(96)00348-7.

4. Sleight A. W., Gillson J. L., Weiher J. F. (1974) Crystal structures and properties of bismuth rhenium oxides *Inorganic Chemistry*. Vol. 13, No. 3. P. 617–626. https://doi.org/10.1021/ic50133a023.

5. T. Fries G. Lang, S. Kemmler-Sack (1996) Defect fluorite structures in the Bi-rich part of the system Bi_2O_3 Re_2O_7 *Solid State Ionics* Volume 89, Issues 3-4,2 August, Pages 233-240 https://doi.org/10.1016/0167-2738(96)00272-X

6. Neeraj Sharma, Ray L. Withers, Kevin S. Knight, Chris D. Ling (2009) Structure, crystal chemistry and thermal evolution of the δ-Bi_2O_3-related phase Bi_9ReO_{17} *Journal of Solid State Chemistry* Volume 182, Issue 9, September, Pages 2468-2474 https://doi.org/10.1016/j.jssc.2009.07.008

7. Mark R. Johnson, Ivana Radosavljević Evans (2013) The mechanism of oxide ion conductivity in bismuth rhenium oxide, $Bi_{28}Re_2O_{49}$ *Solid State Ionics* Volume 244, 1 August, Pages 35-39 https://doi.org/10.1016/j.ssi.2013.05.004

8. Rietveld H. M. (1969) A profile refinement method for nuclear and magnetic structures *Journal of Applied Crystallography.* Vol. 2, No. 2. P. 65–71. https://doi.org/10.1107/S0021889869006558.

9. Database PDF-2 від International Centre for Diffraction Data https://www.icdd.com

10. Dr. H. A. Harwig (1978) On the Structure of Bismuthsesquioxide: The α, β, γ, and δ-phas *Zeitschrift für anorganische und allgemeine Chemie Vol.444 p.151-166.* https://doi.org/10.1002/zaac.19784440118

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