

## Synthesis of minerals

### Khanin D. A.<sup>1,2</sup>, Erofeeva K. G.<sup>3,1</sup> Desalination of sulphate of chrome from chlorite and talc-chlorite rocks.

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**Abstract.** The object of research is talc-chlorite and chlorite rocks of chromate deposits in the Urals. The paper presents the results of laboratory studies of the leaching of chromium from rocks and minerals by water and sulfuric acid solution at atmospheric pressure with constant air aeration or without it. The influence of particle size of rock, its mineral composition, pH and the rate of aeration of the solution on the degree of extraction of  $\text{Cr}^{6+}$  in the liquid phase in the processing of samples with sulfuric acid of different concentrations has been studied

**Keywords:** *chromium, talc-chlorite rock, oxidation zone, desalination of chrome, sulphate dissolution.*

Chromates are not common natural chemical mixture. In Russian region chromates are well aware only in the Ural where they were primarily detected at the mid-to-late XVII century. Investigation of chromates began of chrocoites that were discovered in the Berezovskoe gold ore field oxidation zone located at surrounding area of Ekaterinburg. Four new minerals from this mineralogical class – vauquelinite, phoenicochroite, embreyite and cassedanneite, were described at the same place eventually and the fornacite was found. In the Middle Ural aside from the Berezovskoe gold deposit chromatic mineralizing identified in oxidation zones of quartz-sulphide veins on Tochilnaya, Svinechnaya and Sukhoviyaz hills and on Pervomaysko-Zverevskoe, Blagodatnoe and Sverdlovskoe deposits as is also in south Ural (Trebiatskoe deposit) (Ushkin et al., 1986). All places have the same geological settings and chromatic mineralization limited to hypergenesis zone that develop through contacts of sulphide-bearing quartz veins and meta-ultrabasite rocks. In some instances few researchers (Avdonin et Polenov, 2004; Kleimanov et al, 2005) supposed meta-ultrabasite rocks as chrome source. For this process investigation samples of listvenites, talc-chlorite and talc-carbonate rocks from Tochilnaya and Svincovaya hills and Berezovskoe deposit were selected. Listvenites consist of carbonates (30-40%), quartz (30%) and micas (10-20%). Chloritic rocks almost completely consist of chlorite with talc (10%) and accessory spinel. Talc-chlorite rocks consist of chlorite (30-50%), talc (40-50%) and

chromspinelides (less than 5%). In chloritic and talc-chloritic rocks chrome content reaches 0.3 and 0.4 mas. % respectively and in listvenites – up to 0.2 mas.%. The main chrome-concentrator minerals among hypogenet minerals are chromspinelides and layered aluminosilicates (mica and chlorite) that develop by chromspinelides. In chlorite concentrations of the  $\text{Cr}_2\text{O}_3$  can vary in wide-range from 0.3 mas. % on removal from grains of spinel till 2.4 mas.% in chlorite that develops by grains of chromspinelide.

Speed identification and capability of chrome yield from different aluminosilicates (mica and chlorite) in dependence of aeration rate and dissolving agent were the purpose of this work. Few experiments in chrome desalination from chlorites and micas driven by distillate water or sulphuric acid that are in oxidation zones of sulphide ore minerals were conducted. Crushed chippings of rocks 5-10 mm in size were laid pass on the strong sulphuric acid or in distillate water. All samples were divided into two groups. First group of samples were aerated and the second were not. Experiment lasted for 30 days.

Experiment was identified that in solution of strong sulphuric acid with constant aeration chrome concentrations increase from 1 (in pure sulphuric acid (Table, column 1) to 220 ppm (Table, column 3) while chrome concentrations increase only up to 70 ppm (Table, column 2) in solutions without aeration. Under this circumstance significant removal of Ni, V, Mn from chlorite and associated talc has been observed. In solution of distillate water don't happen chrome desalinizing. In listvenites further occur negligible micas decomposition under the influence of sulphuric acid however chrome concentration in solution slightly escalate (Table, column 4). Local dissolution of carbonates with sulphuric acid is either observed. After sulphuric acid influence concentrations  $\text{Cr}_2\text{O}_3$  in chlorite don't exceed 0.3 mas. % and near grains of spinel – 0.8 mas. %. Chrome concentrations in micas don't most nearly vary.

**Table. Solution composition (ICP-MS data)**

Elements	1	2	3	4
Ti	-	1	2	-
V	-	-	10	-
Cr	1	70	220	10
Mn	-	10	20	20
Co	-	1	2	1
Ni	-	5	40	30
Cu	1	2	2	1
Zn	-	3	3	1

*Comments:* All concentrations in ppm. Dash indicates that element concentrations lower than ICP-MS detection limit. 1. sulphuric acid, 2. chloritic rock, experiment without aeration; Experiments with constant flowing aeration: 3. chloritic rock, 4. listvenite.

Experiment results make it clear that at first chrome removes from carbonate-free rocks in which chlorite is widespread (up to 99%). At the same time constant flowing aeration is an important factor that promotes the process acceleration and apparently oxidation  $\text{Cr}^{3+}$  in  $\text{Cr}^{6+}$ .

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**Kovalskaya T.N., Varlamov D.A., Kalinin G.M., Kotelnikov A.R. The synthesis of gallic analogues of feldspars in the  $\text{K}_2\text{O}-\text{Na}_2\text{O}-\text{CaO}-\text{Ga}_2\text{O}_3-\text{SiO}_2$  system.**

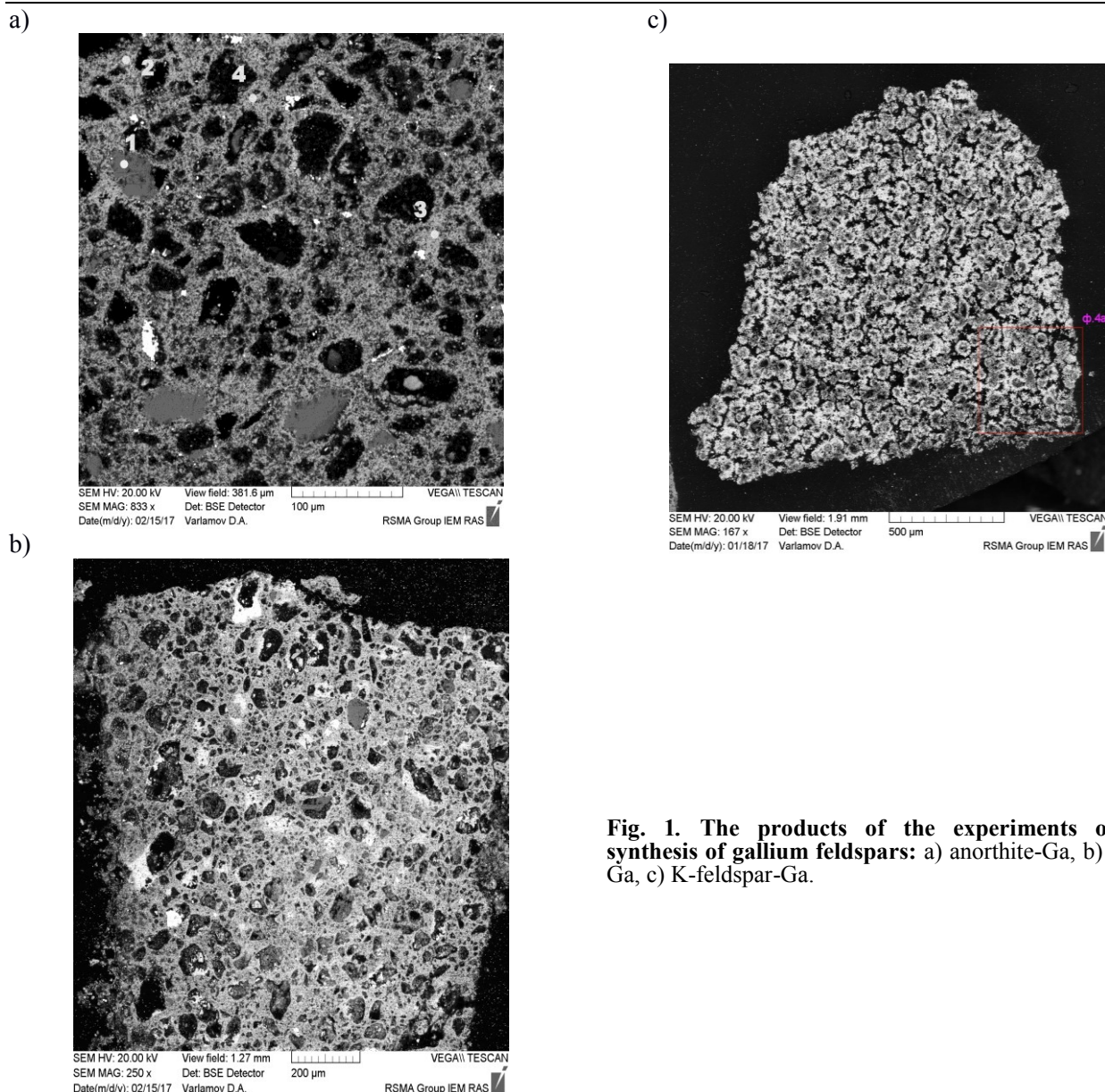
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**Abstract.** Gallium is a rare element and it's own gallium minerals, as well as high contents of this element in other phases, are extremely rare. As a result of the synthesis wide range of Ga epidote compounds was obtained. This paper is devoted to the synthesis of the extreme members of a ternary solid solution anorthite-Ga, albite -Ga and K-Fsp-Ga. As the result of synthesis the crystals of gallium feldspars were obtained.

**Keywords:** gallium, feldspars, synthesis, hydrothermal conditions, experimental study, solid solutions.

As gallium is a trace element its own minerals are rare, and its silicates are scarcely known. The experimental investigations on the synthesis of gallium-containing silicates and aluminosilicates at various P-T conditions began to be carried out with the discovery of epidotes and allanites rich in gallium in the Tykotlov Deposits in the Nether-Polar Urals (18 weight %) (Varlamov et al., 2010). In the years of 2011-2016 gallium epidotes of different composition were found (a solid solution of epidote - gallium epidote in a wide range of compositions), and a "supergallium" epidote in which all the  $\text{Al}^{3+}$  and  $\text{Fe}^{3+}$  were totally substituted for  $\text{Ga}^{3+}$ . Thereby the ability of gallium to be a part of the structure of silicates and aluminosilicates was proved (Kovalskaya et al., 2014, 2015, 2016). For every composition was determined a particular unit cell. In the sequence of experiments on the synthesis of epidotes at  $T=600^\circ\text{C}$  and  $P=4\text{ kbar}$  anorthite -Ga was detected among the by-products. Therefore a decision to investigate the triple system of solid solutions of albite-Ga – anorthite-Ga – K-feldspar-Ga. The first to synthesise gallium feldspars was Peninghaus (Peninghaus, 1980). Only the synthesis parameters were different from those applied in this investigation.

For the time being the endmembers of the solid solutions albite-Ga, anorthite-Ga and K-feldspar-Ga. The synthesis of gallium feldspars was carried out in two steps. The first was concerned with the synthesis of stoichiometric glass of a required composition at atmospheric pressure and  $T=1200^\circ\text{C}$  in platinum ampoules inside a high-temperature furnace Ko-14 for 3 hours at a stretch followed by quenching. As source materials were used  $\text{Na}_2\text{CO}_3$ ,  $\text{K}_2\text{CO}_3$ ,  $\text{CaCO}_3$ ,  $\text{Ga}_2\text{O}_3$  и  $\text{SiO}_2$  of two modifications loosened natural quartz and amorphous  $\text{SiO}_2$  obtained from tetraorthoethylsilicate. In the second case the obtained glasses were more homogeneous, in the case of using quartz little pieces of it can be found in the glass. As the outcome of the first step homogeneous glasses of the appropriate composition, suitable for the further decrystallisation.



**Fig. 1.** The products of the experiments on the synthesis of gallium feldspars: a) anorthite-Ga, b) albite-Ga, c) K-feldspar-Ga.

**Table 1.** The compositions of the synthetic gallium feldspars and its crystallochemical equivalents.

Wt. %	Ga anorthite	Ga albite	Ga-K-Fsp	F.u.	Ga anorthite	Ga albite	Ga-K-Fsp
SiO <sub>2</sub>	34.32	57.68	55.78	Si <sup>4+</sup>	2.05	2.93	2.98
Ga <sub>2</sub> O <sub>3</sub>	47.19	31.9	29.77	Ga <sup>3+</sup>	1.85	1.04	1.01
CaO	17.95	0.0	0.0	Ca <sup>2+</sup>	1.14	0	0
K <sub>2</sub> O	0.02	0.00	14.78	K <sup>+</sup>	0	0	1.01
Na <sub>2</sub> O	0	10.41	0	Na <sup>+</sup>	0	1.03	0
Sum	99.49	99.99	100				

**Key-takeaways:** under geothermal conditions were synthesised gallium-containing analogues of the following feldspars: albite, anorthite and Ga-albite – Ga-K-feldspar, in the composition of which Ga<sup>3+</sup> takes up the position of Al<sup>3+</sup>. During the future experimental investigations using this approach the intermediate terms of the solid solutions of Ga-albite – Ga-anorthite and Ga-albite – Ga-K-feldspar will be synthesised, and also the parameters of lattice cells for feldspars of every particular composition will be defined.

The second step of the synthesis of gallium feldspars was concerned with decrystallisation of the earlier obtained stoichiometric glasses at T=600°C and P=2kbar. The whole series of experimental investigation took 10 days. The synthesis was carried

out in platinum ampoules, in a high-temperature gas furnace. As a mineralising agent for the synthesis of Ga-albite – NaCl, Ga – anorthite – CaCl<sub>2</sub>, Ga-K-feldspar – KCl 1M solutions were used. The solutions were chosen at the ratio of 1:10 to the solid



phase. The products of the experimental investigations were studied with the help of the scanning electron microscope Tescan VEGA-II XMU, an energy-dispersive spectrometer INCA Energy 450 and a wavelength-dispersive spectrometer Oxford INCA Wave 700. The products of the experiments (*figures 1,2,3*) are fine acicular crystals of gallium-containing feldspars. The compositions of the obtained Ga-feldspars are given in the *table 1*.

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**Hydrothermal synthesis and crystal structures of the new bismuth and nickel oxophosphates. UDC 548.736.6**

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**Abstract.** The new oxophosphates: [O<sub>2</sub>Bi<sub>3</sub>]O(PO<sub>4</sub>) (**I**), Ni(BiO)<sub>2</sub>(PO<sub>4</sub>)(OH) (**II**) and KBi<sub>4</sub>{Ni<sub>2</sub>O<sub>4</sub>(PO<sub>4</sub>)<sub>3</sub>} (**III**) were synthesized by a hydrothermal method in the Bi(OH)<sub>3</sub>–NiCO<sub>3</sub>–K<sub>2</sub>CO<sub>3</sub>–K<sub>3</sub>PO<sub>4</sub> system (*T* = 690-700K, *P* = 480-500 atm) and studied by single-crystal X-ray diffraction. The structures of the oxophosphates were refined in the anisotropic approximation of the atomic displacement parameters to final *R*1 = 0.0410(**I**), 0.0409(**II**), 0.0576(**III**). The comparative crystal chemical analysis of a series of fluorite-like bismuth oxophosphates is confirmed that the new bismuth oxophosphate (**I**) is the phase

derivative from [O<sub>4</sub>Bi<sub>5</sub>]O<sub>0.5</sub>(PO<sub>4</sub>)<sub>2</sub> with ionic conductive properties. The namibite type structure of nickel, bismuth oxophosphate (**II**) contains infinite chains {Ni(OH)(PO<sub>4</sub>)}<sub>∞</sub> built of corner-sharing NiO<sub>6</sub> octahedra. The new layer potassium, bismuth, nickel oxophosphate (**III**) is expected to be paramagnetic with very weak antiferromagnetic exchange interactions.

**Keywords:** *bismuth oxophosphates; oxo-centered units; hydrothermal synthesis; single crystal X-ray diffraction; magnetic properties.*

Bismuth and transition metal ions oxosalts are well-known classes of inorganic compounds that attract interest due to a wide range of physical and chemical properties (Liu, 2012). Compounds containing magnetic ions in the high-spin state (Cu<sup>2+</sup> or Ni<sup>2+</sup>) can be potential magnetic materials. Many of these compounds belong to the Bi<sub>2</sub>O<sub>3</sub>–MO–X<sub>2</sub>O<sub>5</sub> ternary system (*M* = divalent metals; X = P, As, V) (Aliev, 2015). In nature phosphates usually associated with granite pegmatites being secondary minerals of the hydrothermal stage of pegmatite development or formed in the hypergenesis zone, therefore, the synthesis of bismuth and nickel phosphates was carried out under hydrothermal conditions. The modelling of natural processes is necessary for the understanding of geochemical and crystal chemical laws and behaviour of bismuth and nickel in the process of crystal formation and also for the synthesis of analogues to minerals and single crystals with predetermined properties. The conduct of the process of synthesis of special purpose bismuth and nickel compounds will give the opportunity to reveal the interconnections between the conditions of formations, crystal structures and properties. Phosphate minerals are dated for the post-magmatic formations which developed in the presence of H<sub>2</sub>O and a wide variety of cations. In this regard features of their crystallization are considered in the Bi(OH)<sub>3</sub>–NiCO<sub>3</sub>–K<sub>2</sub>CO<sub>3</sub>–K<sub>3</sub>PO<sub>4</sub>–B<sub>2</sub>O<sub>3</sub>–H<sub>2</sub>O system. Experiments were carried out in the presence of mineralizers of K<sup>+</sup>, CO<sub>3</sub><sup>2-</sup>, B<sub>2</sub>O<sub>3</sub> (20 wt.% at equal ratio of components) on which pH-solution values depend (Gorbov, 1976). The new oxophosphates: [O<sub>2</sub>Bi<sub>3</sub>]O(PO<sub>4</sub>) (**I**), Ni(BiO)<sub>2</sub>(PO<sub>4</sub>)(OH) (**II**) and KBi<sub>4</sub>{Ni<sub>2</sub>O<sub>4</sub>(PO<sub>4</sub>)<sub>3</sub>} (**III**) were synthesized by a hydrothermal method. Standard Cu-lined stainless steel autoclave of 16 ml capacity was used. The coefficient of the autoclave filling was selected so that pressure was constant. The synthesis was carried out at the general pressure of 480-500 atm in the temperature range from 690 K to 700 K. The bottom temperature-point was limited by kinetics of the chemical reaction while the upper point was limited by equipment characteristics. The experiment duration is 20 days and it corresponds to full completion of the chemical reaction. The following

Compound	The unit cell parameters			Space group, <i>Z</i>	<i>R</i> <sub>1</sub>
	<i>a</i> , Å <i>α</i> , °	<i>b</i> , Å <i>β</i> , °	<i>c</i> , Å <i>γ</i> , °		
[O <sub>2</sub> Bi <sub>3</sub> ]O(PO <sub>4</sub> ) ( <b>I</b> )	5.684 78.96	7.033 77.86	9.158 68.99	<i>P</i> $\bar{1}$ , 2	0.0410
Ni(BiO) <sub>2</sub> (PO <sub>4</sub> )(OH) ( <b>II</b> )	6.322 90.48	6.904 107.22	7.564 110.76	<i>P</i> $\bar{1}$ , 1	0.0409
KBi <sub>4</sub> Ni <sub>2</sub> (PO <sub>4</sub> ) <sub>3</sub> O <sub>4</sub> ( <b>III</b> )	13.632 90.00	19.610 90.00	5.438 90.00	<i>Pnma</i> , 4	0.0576

**Table.** The crystal data of the new oxophosphates

analytical-grade compounds were used: Bi(OH)<sub>3</sub>, NiCO<sub>3</sub>, K<sub>2</sub>CO<sub>3</sub>, K<sub>3</sub>PO<sub>4</sub>, B<sub>2</sub>O<sub>3</sub>. The synthesis was carried out with the Bi<sub>2</sub>O<sub>3</sub> : NiO : K<sub>2</sub>O : P<sub>2</sub>O<sub>5</sub> : B<sub>2</sub>O<sub>3</sub> ratio 1 : 1 : 1 : 1 : 1, and pH = 6-7. The presence of

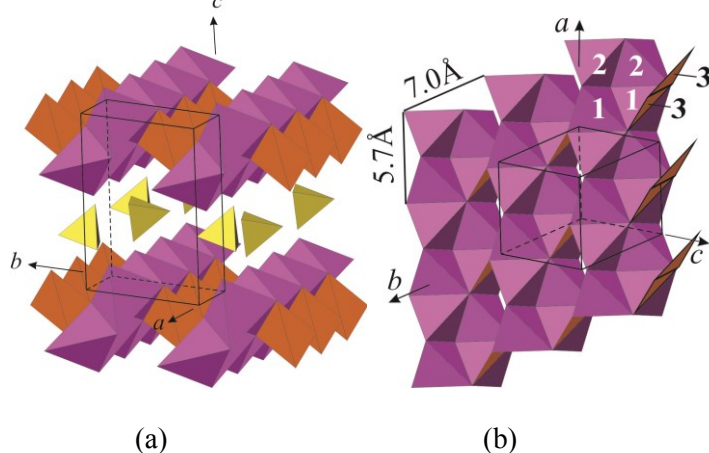
boric acid in natural phosphate systems, which promotes active migration of elements, also maintains close to neutral pH-solution values. In addition, the presence of B<sub>2</sub>O<sub>3</sub> as a buffer can slow down the supply of substances and thus contribute to the simultaneous synthesis of complex compounds with cationic composition. Final cooling after synthesis to room temperature was done in 24 h. The precipitate was separated by stock solution filtering, washed several times with hot distilled water and finally dried at room temperature for 12 h. According to optical microscopy study obtain three types of crystals, different in appearance (morphology, color), and in composition and single crystal X-ray analysis. The structures of the oxophosphates were refined in the anisotropic approximation of the atomic displacement parameters to final *R*<sub>1</sub> = 0.0410(**I**), 0.0409(**II**), 0.0576(**III**). The main crystal data and results of crystal structures refinement are presented in the table. In the structures of the new oxophosphates the so-called 'additional' oxygen atoms uninvolved in the formation of PO<sub>4</sub> tetrahedra are found. These atoms enter into the coordination of bismuth and nickel atoms and participate in the connection of their polyhedra. Thus, four metal atoms share oxygen atoms forming its tetrahedral

environment. This specific feature indicates that there are complexes of oxo-centered tetrahedra, so that the new oxophosphates can be described within anion-centered crystal chemistry (Krivovichev, 2013).

**Phase I.** [O<sub>2</sub>Bi<sub>3</sub>]O(PO<sub>4</sub>). Following the traditional description the crystal structure of new bismuth oxophosphate (Volkov, 2016) contains 8(7)-coordinated Bi-atoms and 4-coordinated P-atoms.

Edge-sharing Bi-polyhedra form parallel (001) dense wide layers which alternate with isolated PO<sub>4</sub>-tetrahedra. According to the principles of anion-centered complexes formation, there are three 'additional' oxygen atoms, which centre two tetrahedra (O1 and O2) and one triangle (O3) with bismuth atoms in vertexes in the structure of [O<sub>2</sub>Bi<sub>3</sub>]O(PO<sub>4</sub>).

The anion-centered tetrahedra connected by the rhombus-like flat radical formed by two triangles into parallel (001) layers (Fig. 1a). The extended along *a* double chains [O<sub>2</sub>Bi<sub>3</sub>]<sup>5+</sup> (type **C8**) formed by edge-sharing [OBi<sub>4</sub>]-tetrahedra are the basic structural fragment of the layer (Fig. 1b). The layers alternate with PO<sub>4</sub> tetrahedra placed in interlayer space. The placement of the rhombus-like radicals between the identical along *Tb* chains leads to the *b* parameter 7.03 Å.



**Fig. 1.** The crystal structure of [O<sub>2</sub>Bi<sub>3</sub>]O(PO<sub>4</sub>): (a) alternation of (001) layers and isolated PO<sub>4</sub> tetrahedra in axonometry; (b) three *Tb* identical double chains [O<sub>2</sub>Bi<sub>3</sub>]<sup>5+</sup> formed by [OBi<sub>4</sub>]-tetrahedra around O1, O2 and connected by [OBi<sub>3</sub>]-triangles around O3. The unit cell parameters *a* (5.7Å) and *b* (7.0Å) are shown.

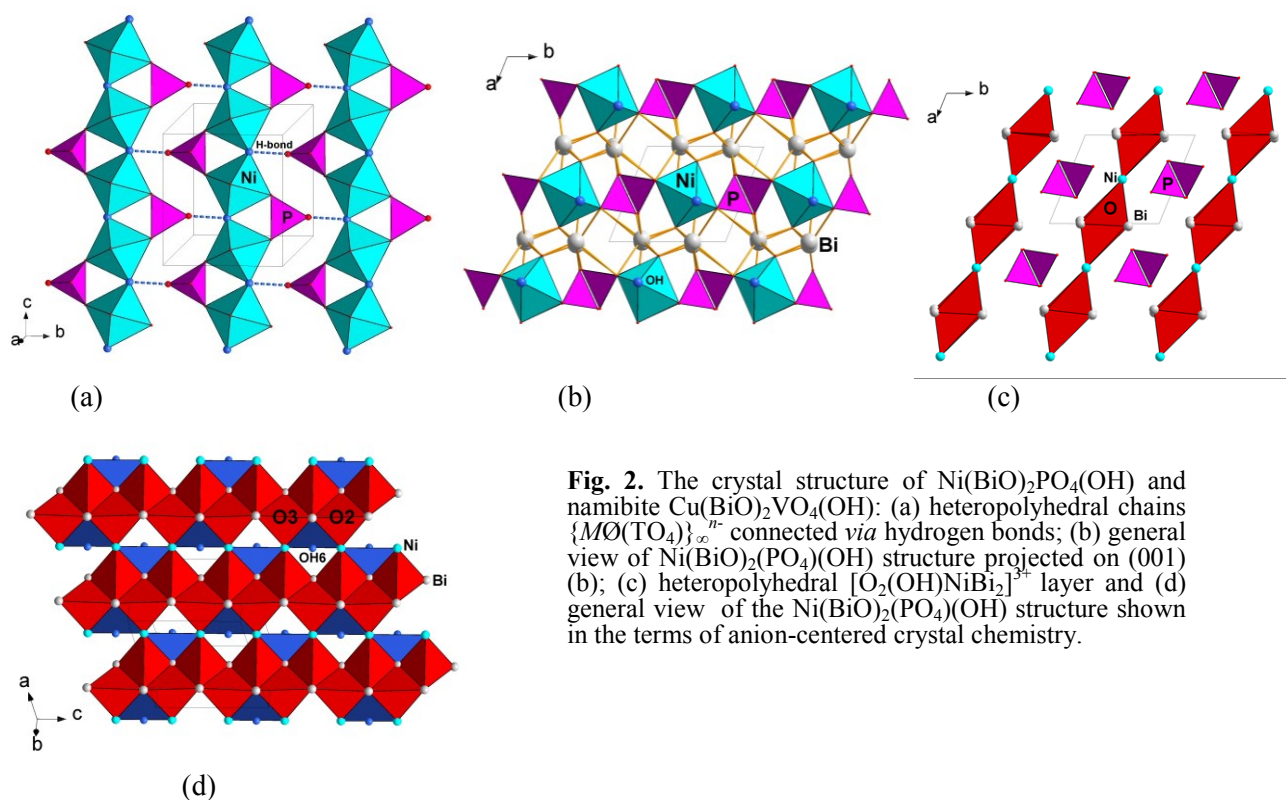
The structure of new oxophosphate [O<sub>2</sub>Bi<sub>3</sub>]O(PO<sub>4</sub>) has no analogs among neither chained nor layered structures of similar composition oxosalts. This oxophosphate takes the intermediate position between oxosalts with mixed

cationic composition and basic formula [O<sub>2</sub>BiM<sub>2</sub>](TO<sub>4</sub>) (Ketatni, 2000) and purely bismuth oxophosphate [O<sub>4</sub>Bi<sub>5</sub>]O<sub>0.5</sub>(PO<sub>4</sub>)<sub>2</sub> (Muktha, 2006). The structures of both oxophosphates contain the basic structural unit: double chains **C8**, which are isolated

from each other in the first structure and connected into layer in the second one. At the structure of new Bi-oxophosphate there are the strongest interatomic bonds along the **C8** chain extension coinciding with fluorite-cube edge and the unit cell parameter **a**. This tendency are noted for similar compounds, in which the unit cell parameters comparable with the fluorite-cube ones. On the other hand the new Bi-oxophosphate can be considered not only as fluorite-like, but also as the phase derivative from  $[O_4Bi_5]O_{0.5}(PO_4)_2$ , in which weak ionic conductivity were noted. This testifies to the possibility of emergency of this property and for the new Bi-oxophosphate  $[O_2Bi_3]O(PO_4)$ .

**Phase II.**  $[O_2NiBi_2](OH)(PO_4)$ . The crystal structure of a new  $Ni(BiO)_2PO_4(OH)$  (Aksenov, 2017) is similar to the structure of namibite  $Cu(BiO)_2VO_4(OH)$  (Kolitsch, 2000) and based on infinite chains  $\{M\emptyset(TO_4)\}_\infty^{n-}$  of vertex-linked octahedra around the magnetic 3d *M*-cations (*M* =

$Ni^{2+}$ ,  $Cu^{2+}$ ; *T* =  $P^{5+}$ ,  $V^{5+}$ , and  $\emptyset = OH^-$ ) going along *c*. Rods are decorated with  $[TO_4]$ -tetrahedra in a staggered arrangement. Adjacent chains are linked along **b** period predominantly *via* hydrogen bonds (Fig. 2a). Heteropolyhedral chains alternates with layers of Bi atoms which are also parallel to (100) (Fig. 2b). The structure of  $Ni(BiO)_2PO_4(OH)$  as well as namibite are characterized by the presence of ‘additional’ oxygen atoms and OH-group and could be described in the terms of anion-centered crystal chemistry.  $[ONiBi_3]$ -tetrahedra linking *via* common edges form double *einer* chain of **C3**-type going along *c*. Oxygen O6 atom belonging to hydroxyl group form  $[ONi_2Bi]$ -triangle and attached additionally to the tetrahedral chain. Condensation of the chains leads to formation of heteropolyhedral  $[O_2(OH)NiBi_2]^{3+}$  layer which are parallel (010) (Fig. 2c). The interlayer space is occupied by isolated  $[PO_4]^{3-}$ -tetrahedra (Fig. 2d).

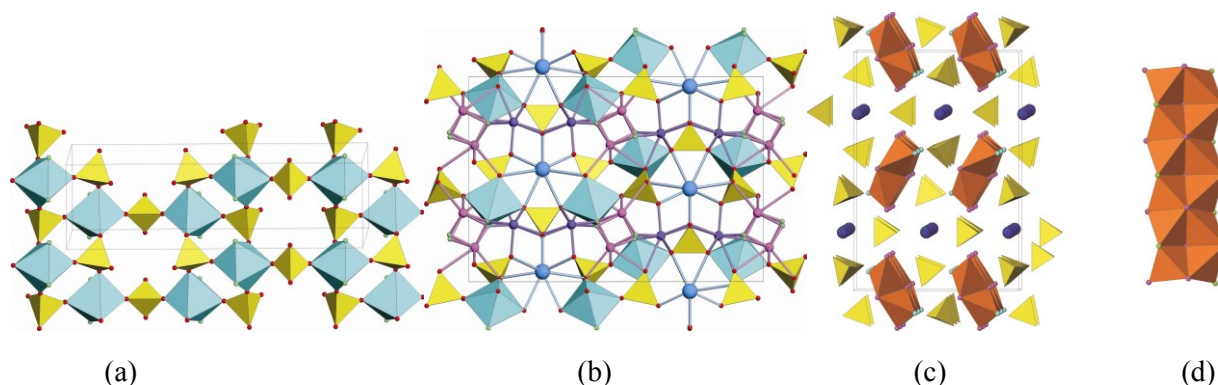


**Fig. 2.** The crystal structure of  $Ni(BiO)_2PO_4(OH)$  and namibite  $Cu(BiO)_2VO_4(OH)$ : (a) heteropolyhedral chains  $\{M\emptyset(TO_4)\}_\infty^{n-}$  connected *via* hydrogen bonds; (b) general view of  $Ni(BiO)_2(PO_4)(OH)$  structure projected on (001) (b); (c) heteropolyhedral  $[O_2(OH)NiBi_2]^{3+}$  layer and (d) general view of the  $Ni(BiO)_2(PO_4)(OH)$  structure shown in the terms of anion-centered crystal chemistry.

**Phase III.**  $K[O_4Ni_2Bi_4](PO_4)_3$ . The crystal chemical formula of the new compound can be written as  $KBi_4\{Ni_2O_4(PO_4)_3\}$  (*Z* = 4); the new nickel–phosphate polyanion is enclosed in braces. The crystal structure of  $KBi_4Ni_2(PO_4)_3O_4$  (Yamnova, 2017) is pseudolayer: its basis is formed by the corrugated  $\{Ni_2O_4(PO_4)_3\}$  heteropolyhedral layer parallel to the (100) plane (Fig. 3a). The layer consists of doubly charged  $[NiO_2(P_1O_4)]$  chains running along the *c* axis and connected by bridging  $P_2O_4$  tetrahedra into the  $[4^48^2]$  network containing four- and eight-membered rings. Along the *a* axis, nickel–phosphate layers alternate with bismuth layers

formed by large  $Bi(1-2)O_7$ -polyhedra. The potassium atoms are enclosed in large  $KO_8$ -polyhedra located between bismuth and wavy nickel–phosphate layers (Fig. 3b). The new oxophosphate can be described within anion-centered crystal chemistry. Based on this concept, double  $[O_2Bi_2Ni]^{4+}$  chains (**C8** type) running along the *c* axis are distinguished in the structure. Each chain consists of edge-sharing  $[OBi_3Ni]$  tetrahedra. Along the *a* axis, the chains alternate with isolated  $PO_4$ -tetrahedra forming the  $\{[O_2Bi_2Ni]_2(PO_4)_2\}^{2+}$  “cationic” block 1 of the structure (Fig. 3c,d).





**Fig. 3.** The crystal structure of  $\text{KBi}_4\text{Ni}_2(\text{PO}_4)_3\text{O}_4$ : (a) corrugated hetero-polyhedral layer  $\{\text{Ni}_2\text{O}_4(\text{PO}_4)_3\}$ ; (b) alternation of nickel-phosphate layers and bismuth layers along  $a$  axis; (c) alternation of  $[\text{O}_2\text{Bi}_2\text{Ni}]^{4+}$  (C8 type) double chains and the isolated  $\text{PO}_4$ -tetrahedra along  $a$  and  $b$  axes; (d) double chains running along the  $c$  axis. Blue circles – atoms K

A similar (but electroneutral) block exists in compounds of general formula  $[\text{O}_2\text{Bi}M](\text{T}^{6+}\text{O}_4)$ , in particular, in the structure of bismuth–zinc oxophosphate  $[\text{O}_2\text{BiZn}_2](\text{PO}_4)$  (Ketatni, 2000). Alteration of the  $\text{Bi}/M^{2+}$  ratio in the chain toward increasing bismuth content results in the positive charge of block 1 compensated by the additional  $\{\text{K}(\text{PO}_4)\}^{2-}$  “anionic” block 2 inserted between blocks 1. Thus, compound  $\text{KBi}_4\text{Ni}_2(\text{PO}_4)_3\text{O}_4$  has a modular structure. Within the approach of anion-centered crystal chemistry, two blocks are distinguished in the structure, namely, the “cationic”  $\{[\text{O}_2\text{Bi}_2\text{Ni}]_2(\text{PO}_4)_2\}^{2+}$  block (containing double chains of edge-sharing oxo-centered tetrahedra) and the “anionic”  $\{\text{K}(\text{PO}_4)\}^{2-}$  block.

The chained and layers structural motives formed of  $[\text{OBi}_4]$  - tetrahedrons and  $[\text{OBi}_3]$  - triangles are most characteristic of the synthesized Bi-containing oxophosphates. The presence of similar fragments (double chains of edge-sharing oxo-centered tetrahedra) in the new bismuth oxophosphates structures explains their simultaneous crystallization.

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