



# Zincovelesite-6N6S, $Zn_3(Fe^{3+}, Mn^{3+}, Al, Ti)_8O_{15}(OH)$ , a new högbomite-supergroup mineral from Jacupica mountains, Republic of Macedonia

Nikita V. Chukanov<sup>1</sup> · Maria G. Krzhizhanovskaya<sup>2</sup> · Simeon Jančev<sup>3</sup> · Igor V. Pekov<sup>4</sup> · Dmitry A. Varlamov<sup>1,5</sup> · Jörg Göttlicher<sup>6</sup> · Vyacheslav S. Rusakov<sup>7</sup> · Yury S. Polekhovskiy<sup>8</sup> · Alexandr D. Chervonnyi<sup>1</sup> · Vera N. Ermolaeva<sup>5</sup>

Received: 18 August 2017 / Accepted: 30 January 2018 / Published online: 9 February 2018  
© Springer-Verlag GmbH Austria, part of Springer Nature 2018

## Abstract

A new mineral species zincovelesite-6N6S with the simplified formula  $Zn_3(Fe^{3+}, Mn^{3+}, Al, Ti)_8O_{15}(OH)$  was discovered in the orogenic zone related to the “Mixed Series” metamorphic complex near the Nežilovo village, Jacupica Mountains, Pelagonia mountain range, Republic of Macedonia. In oxide Zn-Fe-Mn ore, zincovelesite-6N6S forms lenticular aggregates up to  $2 \times 2 \times 0.5$  mm consisting of thin near-coplanar platelets up to  $70 \times 70 \times 1 \mu m^3$  and associated with franklinite, gahnite, hetaerolite, zincchromite, ferricronadite, baryte, As-rich fluorapatite, dolomite, Zn-bearing talc, almeidaite, hydroxycalcioroméite, zircon, quartz, and scheelite. In silicate-baryte zones of the metasomatic rock, uniaxial intergrowths of zincovelesite-6N6S with nežilovite are observed. The new mineral is opaque, black, with brownish-black streak. The lustre is strong submetallic to metallic. The micro-indentation hardness is  $1118 \text{ kg/mm}^2$  which corresponds to Mohs’ hardness *ca.* 6½. Zincovelesite-6N6S is brittle, with uneven fracture. No cleavage or parting is observed. The density calculated from the empirical formula is  $5.158 \text{ g/cm}^3$ . In reflected light zincovelesite-6N6S is light grey. The reflectance values [ $R_{\max}/R_{\min}$ , % ( $\lambda$ , nm)] are: 17.1/13.4 (470), 16.5/12.8 (546), 16.2/12.6 (589), 15.6/12.2 (650). The IR spectrum shows the presence of OH groups. According to the Mössbauer spectrum, all iron is trivalent. The Mn K-edge XANES spectroscopy shows that Mn is predominantly or completely trivalent. The average chemical composition is (wt%; electron microprobe, H<sub>2</sub>O determined by gas chromatography of ignition products): MgO 0.97, CuO 0.50, ZnO 30.80, Al<sub>2</sub>O<sub>3</sub> 8.17, Mn<sub>2</sub>O<sub>3</sub> 21.31, Fe<sub>2</sub>O<sub>3</sub> 29.44, TiO<sub>2</sub> 5.28, Sb<sub>2</sub>O<sub>3</sub> 3.74, H<sub>2</sub>O 1.1, total 101.31. The empirical formula based on 16 O atoms is  $H_{1.05}Zn_{3.26}Mg_{0.21}Cu_{0.05}Fe^{3+}_{3.18}Mn^{3+}_{2.32}Al_{1.38}Ti_{0.57}Sb_{0.20}O_{16}$ . Zincovelesite-6N6S is trigonal, probable space group  $P-3m1$ ,  $a = 5.902(2)$  Å,  $c = 55.86(1)$  Å,  $V = 1684.8(9)$  Å<sup>3</sup>,  $Z = 6$ . The strongest lines of the powder X-ray diffraction pattern [ $d$ , Å (I, %) ( $hkl$ )] are: 2.952 (62) (110), 2.881 (61) (1.0.16), 2.515 (100) (204), 2.493 (88) (1.1.12), 2.451 (39) (1.0.20), 1.690 (19) (304, 2.1.16), 1.572 (19) (2.0.28), 1.475 (29) (221). Zincovelesite-6N6S is the first Fe<sup>3+</sup>-dominant member of the högbomite supergroup and, thus, can be considered as a parent species of a new mineral group. The rootname *velesite* is given for the discovery locality near the city of Veles.

**Keywords** New mineral · Zincovelesite-6N6S · Högbomite supergroup · Mössbauer spectroscopy · XANES spectroscopy · IR spectroscopy · Reflectance spectrum · Nežilovo · Jacupica Mountains · Republic of Macedonia

Editorial handling: M. A.T.M. Broekmans

**Electronic supplementary material** The online version of this article (<https://doi.org/10.1007/s00710-018-0555-1>) contains supplementary material, which is available to authorized users.

✉ Nikita V. Chukanov  
chukanov@icp.ac.ru

Extended author information available on the last page of the article

## Introduction

Högbomite-supergroup minerals are trigonal or hexagonal members of the polysomatic series being composed of spinel (*S*) and nolanite (*N*) modules that alternate in a regular way coplanar to (001) (in hexagonal setting); the *S*:*N* ratio is a variable value (Armbruster 2002). Three mineral groups have been distinguished in the högbomite supergroup. In the members of the taaffeite group,  $S = T_2M_4O_8$  and  $N = BeTM_4O_8$  where *T* are tetrahedrally coordinated cations (Mg<sup>2+</sup> or Fe<sup>2+</sup>) and *M* are octahedrally coordinated cations, among which Al prevails. In the members of the högbomite

and nigerite groups,  $S = T_2M_4O_8$  and  $N = TM_4O_7(OH)$  where  $T = Mg^{2+}$  or  $Zn^{2+}$ , and  $M$  are Al-dominant octahedral cations. Högbomite- and nigerite-group minerals are distinguished by the major tetravalent cation in the nolanite module (Ti or Sn, respectively). In the nomenclature approved by the IMA CNMMN (Armbruster 2002), the mineral names have a prefix (magnesio-, zinco- or ferro-) according to the main bivalent cation in the spinel module and a suffix indicating the number of spinel and nolanite modules in the repeat unit.

In this paper we describe a new mineral species zincovelesite-6N6S,  $Zn_3(Fe^{3+}, Mn^{3+}, Al, Ti)_8O_{15}(OH)$ , which is the first  $Fe^{3+}$ -dominant (in octahedral sites) member of the högbomite supergroup. The rootname *velesite* for zincovelesite-6N6S is given for the discovery locality near the city of Veles. The prefix “zinco-” reflects the predominance of Zn among bivalent cations and the suffix “-6N6S” reflects the total number of nolanite (*N*) and spinel (*S*) modules, in accordance with the nomenclature of högbomite-supergroup minerals (Armbruster 2002) and by analogy with magnesiohögbomite-6N6S, magnesionigerite-6N6S and ferronigerite-6N6S. The mineral and its name have been approved by the IMA Commission on New Minerals, Nomenclature and Classification (IMA No. 2017-034). Fragments of the holotype specimen of zincovelesite-6N6S are deposited in the collections of the Fersman Mineralogical Museum of the Russian Academy of Sciences, Moscow, Russia, with the registration number 4787/1, and in the National Institution Macedonian Museum of Natural History, Skopje, Republic of Macedonia, with the registration number PNMG 790.

## Occurrence

Zincovelesite-6N6S was found about 4.5 km NW of the village of Nežilovo and about 25 km WSW of the city of Veles, Republic of Macedonia (41°41' N, 21°25' E). Associated minerals are franklinite, gahnite, hetaerolite, zincochromite, ferricoronadite, baryte, As-rich fluorapatite, dolomite, Zn-bearing talc, almeidaite, hydroxycalcioroméite, zircon, quartz, and scheelite. Zincovelesite-6N6S occurs in the orogenic zone related to the “Mixed Series” metamorphic complex situated Jacupica Mountains belonging to the Pelagonia mountain range.

The “Mixed Series” is a metamorphosed volcano-sedimentary formation composed mainly of albite augen gneisses and meta-rhyolites around which there are lenses of dolomitic marbles metasomatically replaced by a very unusual and complex mineral assemblages (Barić and Ivanov 1960; Ivanov and Jančev 1976; Chukanov et al. 2015). Post-magmatic fluids related to meta-rhyolites are considered as a possible source of a number of specific, ore and rare elements (Pb, Zn, Sb, As, Cu, Ba, REE, etc.) in contact

metasomatic rocks widespread in the Nežilovo area (Jančev 1997). A specific feature of these metasomatic rocks is their formation under highly oxidizing conditions. As a result, the chalcophile elements (S, As, Sb, Zn, Pb) are mainly concentrated in the form of oxides and oxysalts, whereas sulfides and sulfosalts are present only in trace amounts.

Relics of zircon and zincochromite belong to the earliest paragenesis. Thereafter franklinite and hetaerolite crystallized. During the next stage, franklinite and hetaerolite were partly replaced by gahnite to form predominantly franklinite – hetaerolite – gahnite aggregate. Zincovelesite-6N6S crystallized at a relatively late stage of metasomatic processes and probably has a hydrothermal origin. It forms oriented pseudomorphs after zinc spinels and epitaxial overgrowths on their grains. Ferricoronadite is one of the latest minerals in this association: it forms veinlets cross-cutting the spinel and spinel-högbomite zones of Zn-oxide aggregates (Chukanov et al. 2016).

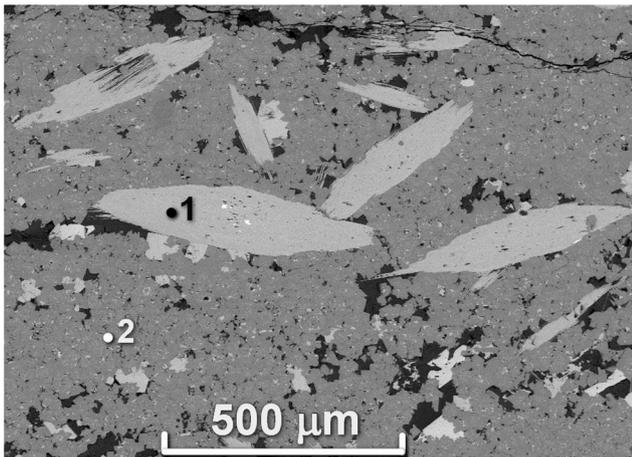
## Physical properties

### General appearance and mechanical properties

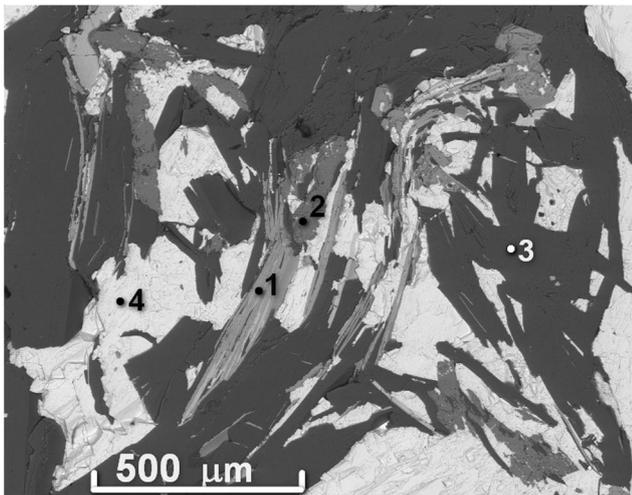
In oxide zones of the metasomatic rock zincovelesite-6N6S forms lenticular aggregates up to  $2 \times 2 \times 0.5$  mm<sup>3</sup> consisting of thin near-coplanar platelets up to  $70 \times 70 \times 1$  μm<sup>3</sup> (Figs. 1, 2). In silicate-baryte zones regular (with parallel *c* axes) intergrowths of zincovelesite-6N6S with nežilovite up to  $0.5 \times 0.5 \times 0.1$  mm<sup>3</sup> are usual (Fig. 3). The new mineral is opaque, its colour is black, and the streak is brownish-black. The lustre is strong submetallic to metallic. The new mineral is brittle. VNH hardness measured by micro-indentation at a load of 200 g ranges from 946 to 1233 kg/mm<sup>2</sup>; the mean value over 4 measurements is 1118 kg/mm<sup>2</sup> which



Fig. 1 Lenticular zincovelesite-6N6S aggregates



**Fig. 2** Lenticular zincovelesite-6N6S aggregates (1) in fine-grained predominantly gahnite matrix (2). Polished section. SEM (BSE) image



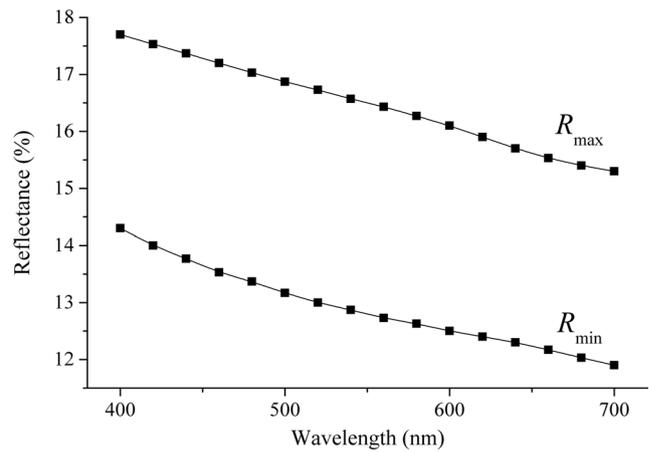
**Fig. 3** Uniaxial intergrowths of zincovelesite-6N6S with nežilovite (1) in association with gahnite (2), Zn-rich phlogopite (3) and baryte (4). Polished section. SEM (BSE) image

corresponds to Mohs' hardness *ca.* 6½. Fracture is uneven; no cleavage or parting is observed.

Density of zincovelesite-6N6S calculated from the empirical formula is equal to 5.158 g/cm<sup>3</sup>. Density could not be measured because of the lack of heavy liquids with densities above 5 g/cm<sup>3</sup> and tiny sizes of pure, monomineral fragments.

### Reflectance spectroscopy in the visible range

Reflectance values ( $R_{max}/R_{min}$ ) for zincovelesite-6N6S (Fig. 4) have been measured in air using a MSF-21 microspectrophotometer (LOMO company, St. Petersburg, Russia) with the monochromator slit width of 0.4 mm and beam



**Fig. 4** Reflectance spectra of zincovelesite-6N6S ( $R_{max}/R_{min}$ )

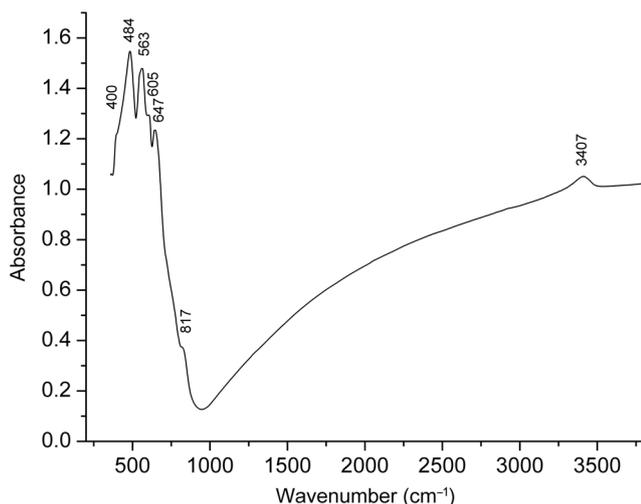
**Table 1** Reflectance values for zincovelesite-6N6S

$\lambda$ , nm	$R_{max}$	$R_{min}$
400	17.7	14.3
420	17.5	14.0
440	17.4	13.7
460	17.2	13.6
<b>470</b>	<b>17.1</b>	<b>13.4</b>
480	17.0	13.3
500	16.9	13.2
520	16.7	13.0
540	16.6	12.8
<b>546</b>	<b>16.5</b>	<b>12.8</b>
560	16.4	12.8
580	16.3	12.6
<b>589</b>	<b>16.2</b>	<b>12.6</b>
600	16.1	12.5
620	15.9	12.4
640	15.7	12.3
<b>650</b>	<b>15.6</b>	<b>12.2</b>
660	15.5	12.2
680	15.4	12.0
700	15.3	11.9

Note: Reflectance values for four wavelengths recommended by the IMA Commission on Ore Microscopy are given in bold type

diameter of 0.1 mm. SiC (Reflection standard 474,251, No. 545, Germany) was used as a standard.

Zincovelesite-6N6S is anisotropic, with  $\Delta R_{589} = 3.6\%$ . The colour in reflected light is light grey. Internal reflections are not observed. The reflectance values ( $R_{max}/R_{min}$ ) are given in Table 1.



**Fig. 5** Powder infrared absorption spectrum of zincovelesite-6N6S

### Infrared absorption spectroscopy

In order to obtain an IR absorption spectrum, zincovelesite-6N6S powder was mixed with anhydrous KBr, pelletized, and analyzed using an ALPHA FTIR spectrometer (Bruker Optics) at a resolution of  $4\text{ cm}^{-1}$ . 16 scans were collected. The IR spectrum of an analogous pellet of pure KBr was used as a reference.

The IR spectrum of zincovelesite-6N6S (Fig. 5) contains bands of O–H-stretching and  $M\cdots\text{O}$ –H bending vibrations (at  $3407$  and  $817\text{ cm}^{-1}$ , respectively). The strong bands in the range  $360$ – $650\text{ cm}^{-1}$  correspond to  $M\cdots\text{O}$ -stretching vibrations ( $M = \text{Fe}^{3+}$ ,  $\text{Mn}^{3+}$ ,  $\text{Al}$ ,  $\text{Ti}$ ).

### $^{57}\text{Fe}$ Mössbauer spectroscopy

The Mössbauer spectra were measured on an MS1104Em spectrometer of electromechanical-type operating in the

constant acceleration mode with a triangular form of the variation of the Doppler velocity of the source with respect to the absorber.  $^{57}\text{Co}$  nuclei in the Rh matrix served as a source. The Mössbauer spectrometer was calibrated using a standard  $\alpha$ -Fe absorber. The measurements were performed in transmission geometry at room temperature.

The Mössbauer spectrum of zincovelesite-6N6S (Tables 2, 3; Figs. 6, 7) shows that all iron is trivalent, and most part of  $\text{Fe}^{3+}$  has octahedral coordination. Two models have been considered. Data obtained by fitting of the Mössbauer spectrum by two pseudo-Voigt doublets (Fig. 6) and from the reconstruction of the hyperfine parameter distribution (Fig. 7) are given in Tables 2 and 3, respectively.

### Mn K-edge XANES spectroscopy

Mn K-edge XANES spectroscopy has been applied to determine mean Mn valence in zincovelesite-6N6S. The spectra were recorded at the X-ray beamline of the Synchrotron Radiation Laboratory for Environmental Studies (SUL-X), synchrotron radiation source ANKA (Karlsruhe Institute of Technology, KIT). The storage ring operated at electron energy of 2.5 GeV. The radiation source of the SUL-X beamline is a 27 pole Wiggler. A Si(111) crystal pair has been used as double crystal monochromator with fixed beam height.

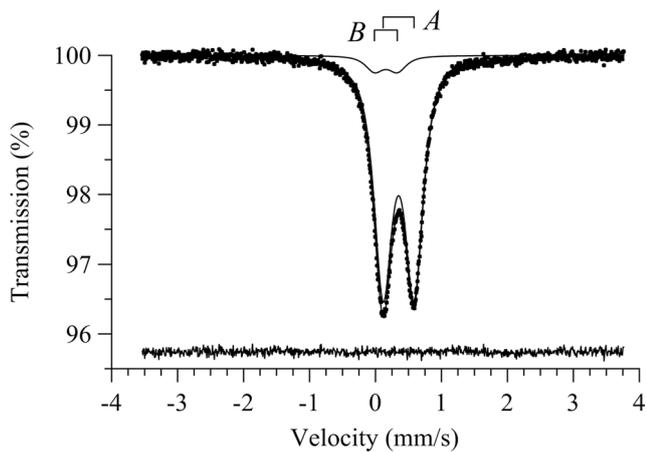
Due to paucity of the sample, a homogeneous pellet (the optimum preparation for XANES spectra measurements in transmission) could not be prepared. Instead few amounts of grinded material was distributed on a Kapton tape which required a micro-focused beam generated by Kirk-Patrick Baez mirrors to the beam sizes at the sample of  $\sim 100\text{ }\mu\text{m}$  (horizontal) and  $\sim 70\text{ }\mu\text{m}$  (vertical). Data have been recorded in transmission with ionization chambers and simultaneously in fluorescence mode (Mn  $K_{\alpha}$  fluorescence emission using a seven element Si(Li) solid state detector, SGX Sorsortech, former Gresham). Fluorescence data were preferred because

**Table 2** Parameters obtained by fitting of the Mössbauer spectrum of zincovelesite-6N6S by two doublets

Quadrupole doublet	Isomer shift, mm/s	Quadrupole splitting, mm/s	Line width, mm/s	Relative area, %	Assignment
A	$0.350 \pm 0.001$	$0.468 \pm 0.001$	$0.327 \pm 0.003$	$93.7 \pm 0.7$	$^{\text{VI}}\text{Fe}^{3+}$
B	$0.157 \pm 0.010$	$0.347 \pm 0.016$		$6.3 \pm 0.7$	$^{\text{IV}}\text{Fe}^{3+}$

**Table 3** Average values of the parameters obtained in the reconstruction of the hyperfine parameter distribution for the Mössbauer spectrum of zincovelesite-6N6S

Quadrupole doublet	Isomer shift, mm/s	Quadrupole splitting, mm/s	Line width, mm/s	Relative area, %	Assignment
A	$0.348 \pm 0.002$	$0.468 \pm 0.002$	$0.320 \pm 0.005$	$95.6 \pm 1.5$	$^{\text{VI}}\text{Fe}^{3+}$
B	$0.145 \pm 0.028$	$0.322 \pm 0.035$	$0.320 \pm 0.005$	$4.4 \pm 1.5$	$^{\text{IV}}\text{Fe}^{3+}$



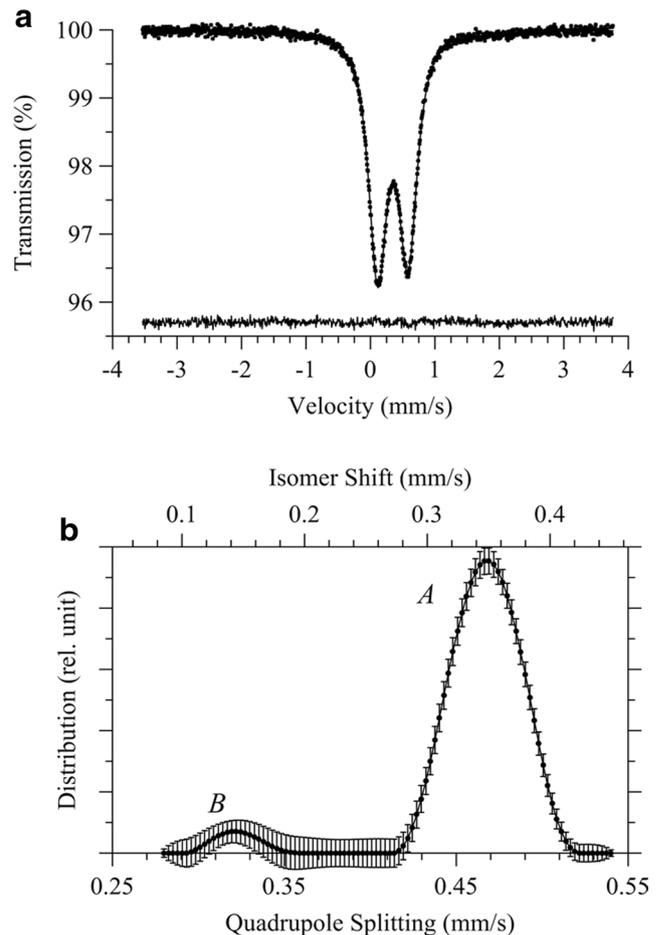
**Fig. 6**  $^{57}\text{Fe}$  Mössbauer spectrum of zincovelesite-6N6S and its fitting by two pseudo-Voigt ( $\alpha=0.206\pm 0.013$ ) quadrupole doublets (A and B)

transmission data are disturbed by unavoidable sample layer inhomogeneity on the tape. Self-absorption correction for the fluorescence data was not necessary because they do not show self-absorption effects, proved by comparison with the transmission data. Energy has been calibrated to 6539 eV (first inflection point of Fe K XANES spectra of a Mn foil measured simultaneously to sample and reference spectra with the second and third ionization chambers.

XANES spectra were recorded in energy steps of 5 eV from  $-150$  to  $-50$  eV and of 2 eV from  $-50$  to  $-20$  eV prior to the edge, of 0.3 eV from  $-20$  to  $+20$  eV across the edge, and with a  $k$  step of 0.05 from  $k$  2.29 to at least  $k$  8.3 ( $+20$  to about  $+260$  eV) above the edge. To increase the signal to noise ratio, scans have been repeated when sufficient measurement time was available. Spectra were pre- and post-edge background corrected and normalized using the ATHENA program of the Ifeffit software package (Ravel and Newville 2005).

The Mn K XANES spectrum of zincovelesite-6N6S compared to Mn K XANES spectra of Mn(II) and Mn(III) references shows that the rising edge flank plot is close to those of Mn(III) compounds but is shifted to that of  $\text{MnO}_2$  (Fig. 8). Consequently, despite most part of Mn in zincovelesite-6N6S is trivalent, a substantial portion of Mn may be tetravalent.

The Mn K XANES spectrum of zincovelesite-6N6S is similar to the spectrum of hydrohetaerolite  $Zn_2Mn_4O_8 \cdot H_2O$  as it is shown by Farges (2005). The arrangement of Zn tetrahedra and Mn octahedra in hetaerolite (Nogues and Poix 1972) and hydrohetaerolite (McAndrew 1956) is similar to the arrangement of Mn(II) tetrahedra and Mn(III) octahedra in hausmannite ( $\text{Mn}_3\text{O}_4$  with the structure related to that of normal spinels; Jarosch 1987). Based on the spectral similarity of the Mn XANES spectra of zincovelesite-6N6S with those of hydrohetaerolite and hetaerolite, we can conclude



**Fig. 7**  $^{57}\text{Fe}$  Mössbauer spectrum of zincovelesite-6N6S (a) and corresponding hyperfine parameter distribution (b) obtained with pseudo-Voigt ( $\alpha=0.182\pm 0.017$ ) resonant lines

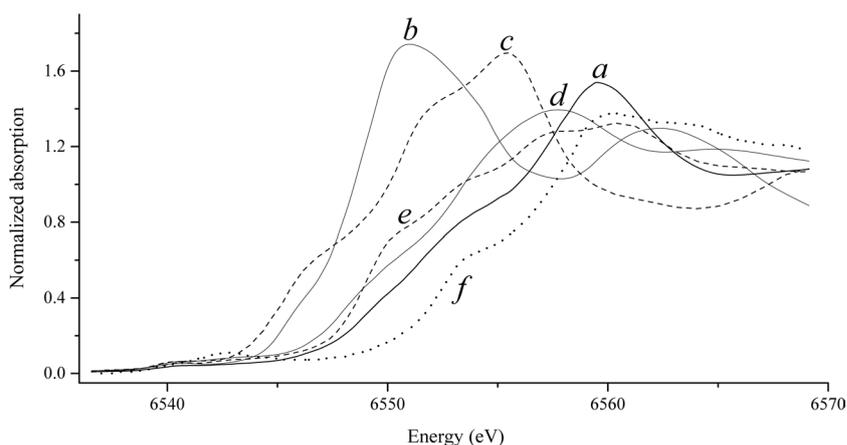
that in all these minerals Zn-centered tetrahedra and Mn(III)-centered octahedra are arranged in a similar way.

### Fe K-edge XANES spectroscopy

Sample preparation and experimental conditions for X-ray absorption spectroscopy at the Fe K edge were the same as for Mn. The Fe  $K\alpha$  fluorescence emission has been recorded for the spectra in fluorescence mode. Energy has been calibrated to 7112 eV with a Fe foil. As for the Mn spectra, self-absorption was not observed and fluorescence emission detection resulted in better data quality. Hence, Fe K-edge XANES spectra measured in fluorescence mode are used here.

The position of the Fe K edge of zincovelesite-6N6S coincide with the edges of the Fe(III) references goethite and hematite which confirms the Mössbauer results of trivalent Fe (Fig. 9a). The low pre-edge peak intensity in the zincovelesite-6N6S Fe K XANES spectrum indicates Fe

**Fig. 8** Mn *K*-edge XANES spectrum of (a) zincovelesite-6*N6S* (thick solid line). The reference spectra of (b) rhodochrosite  $\text{MnCO}_3$  ( $\text{Mn}^{2+}$ ), (c)  $\text{MnO}$  ( $\text{Mn}^{2+}$ ), (d) bixbyite  $\text{Mn}_2\text{O}_3$  ( $\text{Mn}^{3+}$ ), (e) manganite  $\text{MnOOH}$  ( $\text{Mn}^{3+}$ ), and (f)  $\text{MnO}_2$  ( $\text{Mn}^{4+}$ ) are given for comparison



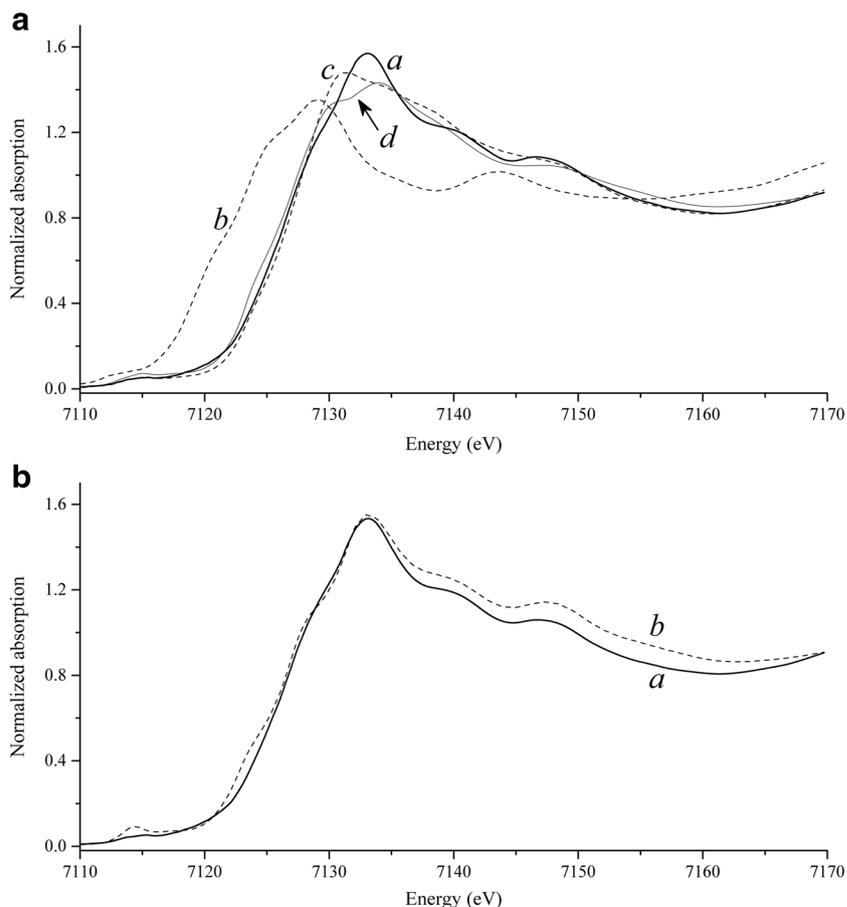
in octahedral coordination in contrast to the high pre-edge intensity in the spectra for maghemite ( $\gamma\text{-Fe}_2\text{O}_3$ ) where a part of the Fe is in tetrahedral coordination with oxygen (Fig. 9b). This observation indicates the occurrence of  $\text{Fe}^{3+}$  in the octahedral *M* position of the h ogbomite structure. The Fe *K* XANES spectrum of zincovelesite-6*N6S* is very close to that of the spinel-type ferrite franklinite  $\text{ZnFe}_2\text{O}_4$  (Nakashima et al. 2007). This means that  $\text{Fe}^{3+}$  occupies octahedral positions in the zincovelesite-6*N6S* structure and,

taking into account chemical composition (see below), is the dominant octahedral cation in this mineral.

### Chemical composition

15 chemical analyses were carried out using an Oxford INCA Wave 700 electron microprobe (WDS mode, 20 kV, 600 pA, 300 nm beam diameter). Contents of

**Fig. 9** a Fe *K* XANES spectra of (a) zincovelesite-6*N6S* compared to reference spectra for (b) w ustite  $\text{FeO}$  ( $\text{Fe}^{2+}$ ), (c) goethite  $\text{FeOOH}$  ( $\text{Fe}^{3+}$ ) and (d) hematite  $\alpha\text{-Fe}_2\text{O}_3$  ( $\text{Fe}^{3+}$ ). b Fe *K* XANES spectra of (a) zincovelesite-6*N6S* and (b) maghemite  $\gamma\text{-Fe}_2\text{O}_3$



**Table 4** Chemical composition for zincovelesite-6N6S (in wt%)

Constituent	Mean	Range	Standard deviation	Probe standard
MgO	0.97	0.34–1.36	0.37	MgO
CuO	0.50	0.27–0.72	0.15	Cu
ZnO	30.80	27.86–33.79	2.10	Zn
Al <sub>2</sub> O <sub>3</sub>	8.17	7.23–8.69	0.50	Al <sub>2</sub> O <sub>3</sub>
Mn <sub>2</sub> O <sub>3</sub> *	21.31	19.72–24.05	1.49	Mn
Fe <sub>2</sub> O <sub>3</sub> *	29.44	26.97–33.44	1.55	Fe
TiO <sub>2</sub>	5.28	3.07–7.97	1.41	Ti
Sb <sub>2</sub> O <sub>5</sub>	3.74	1.24–6.52	1.91	Sb
H <sub>2</sub> O	1.1 ± 0.2			
Total	101.31			

\*According to Mn K-edge XANES and Mössbauer spectroscopic data, Mn and Fe are completely trivalent

other elements with atomic numbers > 8 are below detection limits.

H<sub>2</sub>O content was determined by gas chromatography of products of ignition at 1200 °C with a Vario MICRO cube analyser (Elementar GmbH, Germany). Analytical data are given in Table 4.

The empirical formula (based on 16 O atoms) is H<sub>1.05</sub>(Zn<sub>3.26</sub>Mg<sub>0.21</sub>Cu<sub>0.05</sub>Fe<sup>3+</sup><sub>3.18</sub>Mn<sup>3+</sup><sub>2.32</sub>Al<sub>1.38</sub>Ti<sub>0.57</sub>Sb<sub>0.20</sub>)<sub>Σ11.17</sub>O<sub>16</sub>. Recalculation on 11 metal cations (taking into account that according to Mn K-edge XANES data a part of Mn may be tetravalent) and 16 O atoms gives the following charge-balanced formula: H<sub>1.03</sub>(Zn<sub>3.21</sub>Mg<sub>0.21</sub>Cu<sub>0.05</sub>Fe<sup>3+</sup><sub>3.13</sub>Mn<sup>3+</sup><sub>1.79</sub>Mn<sup>4+</sup><sub>0.49</sub>Al<sub>1.36</sub>Ti<sub>0.56</sub>Sb<sub>0.20</sub>)<sub>Σ11.00</sub>O<sub>16</sub>. The simplified formula is Zn<sub>3</sub>(Fe<sup>3+</sup>, Mn<sup>3+</sup>, Al, Ti)<sub>8</sub>O<sub>15</sub>(OH). The idealized end-member formula is Zn<sub>3</sub>Fe<sup>3+</sup><sub>7</sub>TiO<sub>15</sub>(OH), which requires ZnO 27.37, Fe<sub>2</sub>O<sub>3</sub> 62.66, TiO<sub>2</sub> 8.96, H<sub>2</sub>O 1.01, total 100.00 wt%.

## X-ray crystallography

Single-crystal X-ray diffraction (XRD) studies could not be carried out because aggregates of zincovelesite-6N6S are compact and consist of thin near-coplanar platelets up to 1 μm thick.

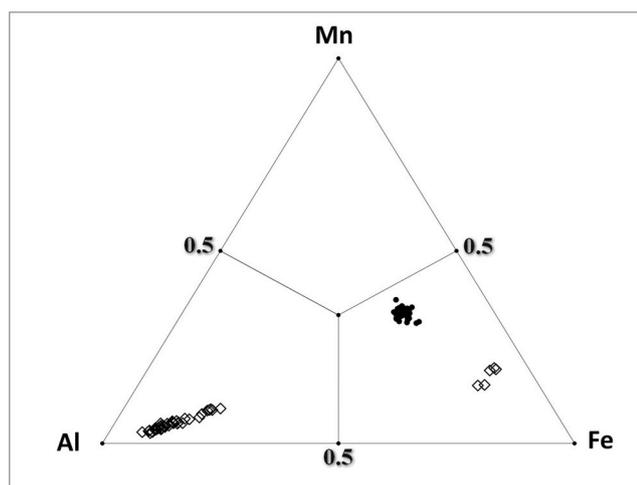
Powder X-ray diffraction data were collected with a Rigaku R-AXIS Rapid II single-crystal diffractometer equipped with cylindrical image plate detector using Debye–Scherrer geometry (*d* = 127.4 mm). Several powdered samples have been prepared, and their purity was tested by means of IR spectroscopy. The sample used for XRD studies does not show IR bands of admixed associated minerals.

**Table 5** Powder X-ray diffraction data for zincovelesite-6N6S

<i>I</i> <sub>meas</sub> , %	<i>d</i> <sub>meas</sub> , Å	<i>d</i> <sub>calc</sub> , Å	<i>hkl</i>	<i>I</i> <sub>meas</sub> , %	<i>d</i> <sub>meas</sub> , Å	<i>d</i> <sub>calc</sub> , Å	<i>hkl</i>
8	13.92*	13.964	004	12	2.239	2.240	2.0.12
5	9.34	9.309	006	2	2.119	2.118	1.0.24
2	8.00*	7.979	007	10	2.061	2.062	2.0.16
2	6.97*	6.982	008	2	1.929	1.929, 1.927	2.0.19, 212
1	6.20	6.206	009	3	1.913	1.914	214
6	5.088	5.090, 5.078	101, 0.0.11	5	1.885	1.885	2.0.20
1	4.932	4.929	103	4	1.859	1.858	1.0.28
7	4.800	4.800	104	5	1.720	1.721	2.0.24
7	4.657	4.655, 4.648	0.0.12, 105	10	1.705	1.704	300
18	4.121	4.124	108	<b>19</b>	<b>1.690</b>	1.691, 1.690	304, 2.1.16
7	3.441	3.441	1.0.12	5	1.654	1.655	308
2	3.107	3.103	0.0.18	16	1.609	1.608	2.0.27
<b>62</b>	<b>2.952</b>	2.951	110	18	1.601	1.600	3.0.12
<b>61</b>	<b>2.881</b>	2.883	1.0.16	16	1.589	1.5887	2.1.20
3	2.794	2.793	0.0.20	<b>19</b>	<b>1.572</b>	1.5725	2.0.28
8	2.716	2.718	118	3	1.551	1.5515	0.0.36
<b>100</b>	<b>2.515</b>	2.514	204	18	1.476	1.4754	220
<b>88</b>	<b>2.493</b>	2.492, 2.491	1.1.12, 205	<b>29</b>	<b>1.475</b>	1.4749	221
<b>39</b>	<b>2.451</b>	2.451	1.0.20	<b>20</b>	<b>1.441</b>	1.4414	2.0.32
11	2.400	2.400	208	3	1.388	1.3877	2.1.28
0.5	2.359	2.359	1.0.21	5	1.313	1.3134	3.1.16

The strongest reflections are given in bold type

\*Diagnostic low-angle reflections that undoubtedly indicate space group *P*-3*m*1, *P*3*m*1 or *P*321 but not *R*-3*m*, *R*3*m* or *R*32



**Fig. 10** Ratios of the contents of trivalent cations (mole fraction) in högbomite-supergroup minerals from the orogenic zone of Jacupica Mountains. Black circles mark samples from oxide rocks (zincovelesite-6N6S), and open squares show samples from silicate-baryte rocks

Data (for CoK $\alpha$ ) are given in Table 5. According to the powder data, zincovelesite-6N6S is trigonal, probable space group  $P\bar{3}m1$ ,  $a = 5.902(2)$  Å,  $c = 55.86(1)$  Å,  $V = 1684.8(9)$  Å<sup>3</sup>,  $Z = 6$  (see below).

## Discussion

The powder X-ray diffraction pattern of zincovelesite-6N6S was well indexed in trigonal cell with  $c$  parameter 55.86 Å which is usually indicative for the 6N6S polysome. The comparison of its crystallographic and powder XRD data (Table 5) with those of all known polysomes of högbomite-supergroup minerals demonstrates the correspondence to the 6N6S form as well. The presence of distinct reflections with  $d = 13.92$ , 8.00, 6.97, 3.44 and 2.72 Å conform to the primitive type of unit cell (space group  $P\bar{3}m1$ ,  $P3m1$  or  $P321$ ) but not rhombohedral one ( $R\bar{3}m$ ,  $R3m$  or  $R32$ ) (see also Pawley plot in Fig. 1S). Three major diagnostic lines (with  $d = 13.92$ , 8.00 and 6.97 Å) observed in the most informative low-angle region, in which reflections can be indexed unequivocally, are marked in Table 5. These reflections could not be attributed to any of associated minerals. Thus by analogy with the

**Table 6** Comparative data for högbomite-supergroup minerals belonging to the 6N6S polysome

Mineral	Zincovelesite-6N6S	Magnesiohögbomite-6N6S*	Magnesionigerite-6N6S	Ferronigerite-6N6S*
Formula	$Zn_3(Fe^{3+}, Mn^{3+}, Al, Ti)_8 O_{15}(OH)$	$(Mg, Al, Fe)_3(Al, Ti)_8 O_{15}(OH)$	$(Mg, Al, Zn)_3(Al, Sn)_8 O_{15}(OH)$	$(Fe^{2+}, Al, Zn)_3(Al, Sn)_8 O_{15}(OH)$
Crystal system	Trigonal	Trigonal	Trigonal	Trigonal
Space group	$P\bar{3}m1$	$R\bar{3}m$	$P\bar{3}m1$ or $R\bar{3}m^{**}$	$R\bar{3}m$
$a$ , Å	5.902	5.7145	5.730	5.530
$c$ , Å	55.86	55.056	55.60	55.60
$V$ , Å <sup>3</sup>	1684.8	1557.0	1581	1473
$Z$	6	6	6	6
Strong lines of the powder X-ray diffraction pattern: $d$ , Å ( $I$ , %)	2.952 (62) 2.881 (61) 2.515 (100) 2.493 (88) 2.451 (39) 1.690 (19) 1.572 (19) 1.475 (29) 1.441 (20)	2.857 (37) 2.825 (67) 2.435 (49) 2.425 (100) 2.009 (31) 1.547 (25) 1.539 (31) 1.429 (61) 1.413 (40)	2.846 (90) 2.624 (20) 2.423 (100) 1.842 (20) 1.639 (30) 1.545 (40) 1.414 (50)	4.399 (31) 4.101 (29) 2.813 (82) 2.765 (64) 2.374 (100) 2.360 (38) 1.605 (24) 1.529 (24) 1.383 (35)
Density, g/cm <sup>3</sup>	5.16 (calc.)	3.77 (calc.)	4.42 (calc.)	4.47 (calc.)
Sources	This work	Hejny & Armbruster, 2002; Armbruster, 2002	Chen Jingzhong et al., 1989; Armbruster, 2002; Yang et al., 2013	Burke et al., 1977; Grey and Gatehouse, 1979; Armbruster, 2002

\*Powder X-ray diffraction patterns calculated from the crystal structure data by Hejny & Armbruster (2002) and by Grey and Gatehouse (1979) for magnesiohögbomite-6N6S and ferronigerite-6N6S, respectively, are given

\*\*Probably, two modifications of magnesionigerite-6N6S exist

structurally studied högbomite-supergroup minerals with primitive unit cells that are characterized by space group  $P-3m1$  (Armbruster 2002), we propose that zincovelesite-6N6S also adopts this space group. Space group  $R-3m$  is a minimal non-isomorphic supergroup of  $P-3m1$ . Thus, any chemical or topological “disturbance” may reduce the symmetry to  $P-3m1$ . The interesting point is that examples of symmetry lowering from the “standard space group” (Hejny and Armbruster 2002) in this supergroup of minerals have not yet been observed.

In all högbomite-supergroup minerals described until now, Al prevails over other trivalent cations ( $Fe^{3+}$ ,  $Mn^{3+}$ ). In the nomenclature approved by the IMA CNMMN, the group name is chosen according to the composition of the aluminium-spinel module and the major tetravalent cation in the nolanite module. If the spinel module is dominated by the gahnite component,  $ZnAl_2O_4$ , the prefix “zinco-” is used (Armbruster 2002). Zincovelesite-6N6S is the first  $Fe^{3+}$ -dominant member of the högbomite supergroup and, consequently, it can be considered as a parent species of a new mineral group with  $Ti^{4+}$  as the major charge-compensating high-valent cation and  $Fe^{3+}$  as the major trivalent cation.

In metasomatic rocks of the Nežilovo area, högbomite-supergroup minerals occur in two types of associations: predominantly oxide and predominantly silicate-baryte ones. In oxide rocks only zincovelesite-6N6S was found. In rocks containing baryte, Zn-rich amphiboles and micas as the major components, both  $Fe^{3+}$ - and Al-dominant högbomite-supergroup minerals (including zincovelesite-6N6S, zincohögbomite-6N6S, and its  $Sb^{5+}$ - and  $Mn^{4+}$ -analogues) occur (see Chukanov et al. 2015). These minerals form separate compositional fields (Fig. 10). Unlike zincovelesite-6N6S, both studied samples of zincohögbomite from Nežilovo (Armbruster et al. 1998; Chukanov et al. 2015) belong to the 2N6S polysome.

Epitaxial intergrowths of högbomite-supergroup minerals with Zn spinels are an obvious result of their structural relationship (i.e., the presence of spinel module in högbomite-type structures). Regular (with parallel  $c$  axes) intergrowths of högbomite-supergroup minerals with nežilovite may be due to close values of their  $a$  unit-cell parameters: 5.74 Å for zincohögbomite-2N6S (Chukanov et al. 2015), 5.90 Å for zincovelesite-6N6S (this study), and 5.85 Å for nežilovite (Bermanec et al. 1996). In addition,  $c$  parameters of zincovelesite-6N6S (55.87 Å) and nežilovite (22.81 Å) are nearly multiples of 11.2–11.4 Å.

Comparative data for högbomite-supergroup minerals belonging to the 6N6S polysome are given in Table 6.

**Acknowledgements** This work was financially supported by the Russian Foundation for Basic Research, grant no. 18-05-00051\_a. The authors thank the Centre for X-ray Diffraction Studies of SPSU for instrumental support.

## References

- Armbruster T (2002) Revised nomenclature of högbomite, nigerite, and taaffeite minerals. *Eur J Mineral* 14:389–395
- Armbruster T, Bermanec V, Zebec V, Oberhänsli R (1998) Titanium and iron poor zincohögbomite-16H,  $Zn_{14}(Al, Fe^{3+}, Ti, Mg)_8Al_{24}O_{62}(OH)_2$ , from Nežilovo, Macedonia: occurrence and crystal structure of a new polysome. *Schweiz Mineral Petrogr Mitt* 78:469–477
- Barić LJ, Ivanov T (1960) Mineralvergesellschaftung in der Umgebung des Dorfes Nežilovo am Jakupica-Gebirge in Mazedonien. *Bulletin Scientifique (Zagreb)* 5:2 (German)
- Bermanec V, Holtstam D, Sturman D, Criddle AJ, Back ME, Scavnicar S (1996) Nežilovite, a new member of the magnetoplumbite group, and the crystal chemistry of magnetoplumbite and hibonite. *Can Miner* 34:1287–1297
- Burke EAJ, Lof P, Hazebroek HP (1977) Nigerite from the Rosendal pegmatite and aplite, Kemiö island, southwestern Finland. *Bull Geol Soc Finland* 49:151–157
- Chen Jingzhong Y, Zhaolu GP, Nicun S, Peng Zhizhong (1989) Discovery and study of pengzhizhongite-6H – a new mineral. *Acta Mineral Sinica* 9(1):20–24 (in Chinese with English abstract)
- Chukanov NV, Jančev S, Pekov IV (2015) The association of oxygen-bearing minerals of chalcophile elements in the orogenic zone related to the “mixed series” complex near Nežilovo, Republic of Macedonia. *Macedonian J Chem Chem Eng* 34(1):115–124
- Chukanov NV, Aksenov SM, Jančev S, Pekov IV, Göttlicher J, Polekhovskiy YuS, Rusakov VS, Nelyubina YuV, Van KV (2016) A new mineral species ferricronadite,  $Pb[Mn^{4+}_6(Fe^{3+}, Mn^{3+})_2]O_{16}$ : mineralogical characterization, crystal chemistry and physical properties. *Phys Chem Miner* 43:503–514
- Farges F (2005) *Ab initio* and experimental pre-edge investigations of the Mn K-edge XANES in oxide-type materials. *Phys Rev B* 71:155109-1-155109-14
- Grey IE, Gatehouse BM (1979) The crystal structure of nigerite-24. *Am Mineral* 64:1255–1264
- Hejny C, Armbruster T (2002) Polysomatism in högbomite: The crystal structures of 10T, 12H, 14T, and 24R polysomes. *Am Mineral* 87:277–292
- Ivanov T, Jančev S (1976) “Nežilovo” – a complex polymetallic deposit of “Franklin Furnace” type in Macedonia. *Proc Yugoslavlian Geol Congress 5, Ljubljana, 1976*, pp. 69–78
- Jančev S (1997) Zn-rich pyroxenes from the occurrences in the mixed series in the upper part of the Babuna River. *Macedonia Geologija (Ljubljana)* 40:283–289
- Jarosch D (1987) Crystal structure refinement and reflectance measurements of hausmannite,  $Mn_3O_4$ . *Mineral Petrol* 37:15–23
- McAndrew J (1956) Observations on hydrotaerolite. *Am Miner* 41:268–275
- Nakashima S, Fujita K, Tanaka K, Hirao K, Yamamoto T, Tanaka I (2007) First-principles XANES simulations of spinel zinc ferrite with a disordered cation distribution. *Phys Rev B* 75:174443-1-174443-8
- Nogues M, Poix P (1972) Effet Jahn-Teller coopératif dans le système  $ZnMn_2O_4$ - $Zn_2SnO_4$ . *Annales de Chemie (Paris)* 1972:301–314 (in French)
- Ravel B, Newville M (2005) ATHENA, ARTEMIS, HEPHAESTUS: Data analysis for X-ray absorption spectroscopy using IFFFIT. *J Synchrotron Radiation* 12:537–541
- Yang Z, Ding K, de Fourestier J, Mao Q, Li H (2013) Fe-rich Li-bearing magnesionigerite-6N6S from Xianghualing tin-polymetallic orefield, Hunan Province, P.R. China. *Mineral Petrol* 107:163–169

## Affiliations

**Nikita V. Chukanov<sup>1</sup> · Maria G. Krzhizhanovskaya<sup>2</sup> · Simeon Jančev<sup>3</sup> · Igor V. Pekov<sup>4</sup> · Dmitry A. Varlamov<sup>1,5</sup> · Jörg Göttlicher<sup>6</sup> · Vyacheslav S. Rusakov<sup>7</sup> · Yury S. Polekhovskiy<sup>8</sup> · Alexandr D. Chervonnyi<sup>1</sup> · Vera N. Ermolaeva<sup>5</sup>**

<sup>1</sup> Institute of Problems of Chemical Physics, Russian Academy of Sciences, Chernogolovka, Moscow Region 142432, Russia

<sup>2</sup> Department of Crystallography, Institute of Earth Sciences, Saint Petersburg State University, Universitetskaya Nab. 7/9, 199034 St., Petersburg, Russia

<sup>3</sup> Faculty of Technology and Metallurgy, Saints Cyril and Methodius University, Ruger Boskovic 16, 1000, Skopje, Republic of Macedonia

<sup>4</sup> Faculty of Geology, Moscow State University, Vorobiev Gory, Moscow 119234, Russia

<sup>5</sup> Institute of Experimental Mineralogy, Russian Academy of Sciences, Chernogolovka, Moscow Region 142432, Russia

<sup>6</sup> Karlsruhe Institute of Technology, Institute for Photon Science and Synchrotron Radiation (IPS), Hermann-von-Helmholtz-Platz 1, D-76344, Eggenstein-Leopoldshafen, Germany

<sup>7</sup> Faculty of Physics, Moscow State University, Vorobiev Gory 119234 Moscow, Russia

<sup>8</sup> Department of Mineral Deposits, Institute of Earth Sciences, Faculty of Geology, St. Petersburg State University, Universitetskaya Nab. 7/9, St., Petersburg 199034, Russia