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Nioboixiolite-(Fe³⁺), (Nb_{0.5}Fe³⁺_{0.5})O₂, a new ixiolite-group mineral from the Eifel paleovolcanic region, Germany

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Running title: Nioboixiolite-(Fe³⁺), a new mineral

Abstract

The new ixiolite-group mineral nioboixiolite-(Fe³⁺), ideally (Nb_{0.5}Fe³⁺_{0.5})O₂, was discovered in nosean sanidinite of the Laach Lake (Laacher See) volcano, Eifel region, Rhineland-Palatinate, Germany. The associated minerals are sanidine, K-bearing albite, nosean, biotite, Nb-rich ilmenite,

Ti-rich magnetite, hercynite, corundum, samarskite-(Y), ekebergite, and columbite-(Fe). Nioboixiolite-(Fe³⁺) forms long prismatic to acicular crystals up to 0.03 × 0.06 × 1 mm and epitaxial intergrowths with ilmenite and intermediate members of the samarskite–ekebergite series. Both colour and streak are black and the lustre is submetallic. The new mineral is brittle, with the Vickers' micro-indentation hardness of 499 kg mm⁻² which corresponds to the Mohs' hardness of 5. No cleavage is observed. The fracture is conchoidal. The calculated density is 5.033 g·cm⁻³. In reflected light, nioboixiolite-(Fe³⁺) is grey, no pleochroism is observed. The reflectance values (R_{\min} , % / R_{\max} , % / λ , nm) are: 14.7/16.4/470, 14.3/15.9/546, 14.1/15.7/589, 14.0/15.8/650. The Raman spectrum shows bands corresponding to stretching vibrations of (Nb,Ti)–O–(Nb,Ti) and (Nb,Ti)–O–Mn²⁺ and the absence of bands of OH groups. The chemical composition is (electron microprobe data, wt.%): MgO 0.41, MnO 3.52, Al₂O₃ 0.42, Cr₂O₃ 0.75, Fe₂O₃ 20.23, TiO₂ 22.26, ZrO₂ 0.76, Nb₂O₅ 51.82, total 100.17. The empirical formula is (Mg_{0.04}Mn²⁺_{0.20})_{Σ0.24}(Al_{0.03}Cr_{0.04}Fe³⁺_{1.01})_{Σ1.08}(Ti_{1.11}Zr_{0.02})_{Σ1.13}Nb_{1.55}O₈ (Z = 1). The strongest lines of the powder X-ray diffraction pattern [d , Å (I , %) (hkl)] are: 3.586 (29) (110), 2.917 (100) (111), 2.503 (18) (002), 2.170 (18) (121), 1.738 (22) (130), 1.689 (26) (221). The crystal structure was determined using single-crystal X-ray diffraction data and refined to $R = 0.0447$. Nioboixiolite-(Fe³⁺) is orthorhombic, space group $Pbcn$, $a = 4.6578(6)$, $b = 5.6230(7)$, $c = 5.0182(5)$ Å, $V = 131.43(3)$ Å³. The new mineral is isostructural with other members of the ixiolite group.

Keywords: nioboixiolite-(Fe³⁺); new mineral; ixiolite group; columbite supergroup; crystal structure; Raman spectroscopy; Laach Lake volcano; Eifel paleovolcanic region.

Introduction

The columbite supergroup, recently approved by the IMA Commission on New Minerals, Nomenclature and Classification (CNMNC; Memorandum 108-SM22 of 20.06.2022; Chukanov *et al.*, 2023a) includes five mineral groups (ixiolite, wolframite, samarskite, columbite, and wodginite groups) and one ungrouped species (lithiotantite). All minerals belonging to the columbite supergroup have the stoichiometry M_xO_{2x} and are topologically related to columbite. Their crystal structures are based on the hexagonal close packing of anions (or close to it) and zig-zag chains of

edge-sharing M-centered polyhedra. In ixiolite-group minerals (space group $Pbcn$, $Z = 4$), all cations are disordered and occupy a single M site. These minerals have the smallest unit cell volume whereas representatives of other groups belonging to the columbite supergroup are characterized by different schemes of cation ordering, which results in changes of symmetry and/or multiplication of unit-cell dimensions.

The new mineral species nioboixiolite-(Fe³⁺), described in this paper, is named in accordance with the current nomenclature of columbite-supergroup minerals (Chukanov *et al.*, 2023). The mineral, its name and symbol (Nbix-Fe³⁺) have been approved by the IMA CNMNC (IMA No. 2024-057). The type specimen is deposited in the collections of the Fersman Mineralogical Museum of the Russian Academy of Sciences, Moscow, Russia with the registration number 6169/1.

Experimental methods and data processing

The Raman spectrum of nioboixiolite-(Fe³⁺) has been obtained from a polished section using an EnSpectr R532 spectrometer based on an OLYMPUS CX 41 microscope coupled with a diode laser ($\lambda = 532$ nm) at room temperature (Moscow State University, Faculty of Geology, Dept. of Mineralogy). Incident laser radiation was linearly polarized. The spectra were recorded in the range from 100 to 4000 cm⁻¹ with a diffraction grating (1800 gr mm⁻¹) and spectral resolution about 4–6 cm⁻¹ (Raman Analyzer Specification). The Rayleigh line was corrected with a cutting-edge low pass filter. Scattered radiation was recorded with a Linear CCD Array detector with 3648 pixels and pixel size 8 $\mu\text{m} \times 200 \mu\text{m}$. The output power of the laser beam was about 16 mW. The diameter of the laser spot on the sample was 15 μm . The backscattered Raman signal was collected with a 40 \times objective; entrance aperture 20 μm wide slit; signal acquisition time for a single scan of the spectral range was 1 s, and the signal was accumulated over 50 scans. Crystalline silicon was used as a standard.

Chemical Analyses (4 points) were carried out on a polished section using an OXFORD INCA Wave 700 electron microprobe operating in WDS mode, 20 kV, 20 nA and a 1 μm beam diameter. Acquisition time was 40s. The SEM microscope is equipped by detectors of secondary and back-scattered electrons based on YAG. The following standards were used: diopside for Mg, albite for Al and pure elements for the other components.

For the determination of the oxidation state of iron in nioboixiolite-(Fe³⁺), a method based on X-ray spectroscopy was used. Recently, X-ray spectroscopic methods have been used as an alternative method for determining oxidation state of Fe (Kupriyanova *et al.*, 2003; Mukhanova *et al.*, 2008; Chubarov *et al.*, 2009; Finkelshtein and Chubarov, 2010; Murashko *et al.*, 2011; Chukanov *et al.*, 2011a,b), and has been applied in this study. The methodology is based on the ratio of intensities of different *K*-lines of X-ray spectra of an element. In this work we used the ratio of the intensities *I* of the FeK β_5 and FeK β_1 lines to determine the value $\delta = [I(\text{FeK}\beta_5)/I(\text{FeK}\beta_1)]$.

The X-ray spectra of the FeK β_5 and FeK β_1 lines were obtained at the D.S. Korzhinskii Institute of Experimental Mineralogy using a scanning electron microscope Tescan Vega XMU equipped with an INCA wave 700 X-ray spectrometer (Oxford INCA Wave 700). Spectra were obtained over 1 minute in WDS mode, 20 kV, 100 nA and beam diameter of 3.5mm. A LiF crystal was used as an analyzer.

X-ray spectra of standards were obtained directly before the collection of data on nioboixiolite-(Fe), the δ value obtained was correlated with δ values obtained from, hematite, Fe₂O₃, magnetite, Fe₃O₄, siderite, FeCO₃, as well as Fe³⁺-bearing atencioite, ideally Ca₂Fe²⁺₃Mg₂Be₄(PO₄)₆(OH)₄·6H₂O (Chukanov *et al.*, 2006), and Fe-bearing perraultite, (Ba,K)₂CaNa(Mn,Fe²⁺,Fe³⁺)₈Ti₄(Si₂O₇)₄O₄(F,OH,O)₆ (Rastsvetaeva *et al.*, 2008), in which the Fe²⁺:Fe³⁺ ratio was determined by means of Mössbauer spectroscopy, in shown in Fig. 1. Its linear approximation corresponds to the equation $\eta = 120.5 \times [I(\text{FeK}\beta_5)/I(\text{FeK}\beta_1)] - 0.4609$. The estimated error of the determination of δ from this correlation is ± 0.08 .

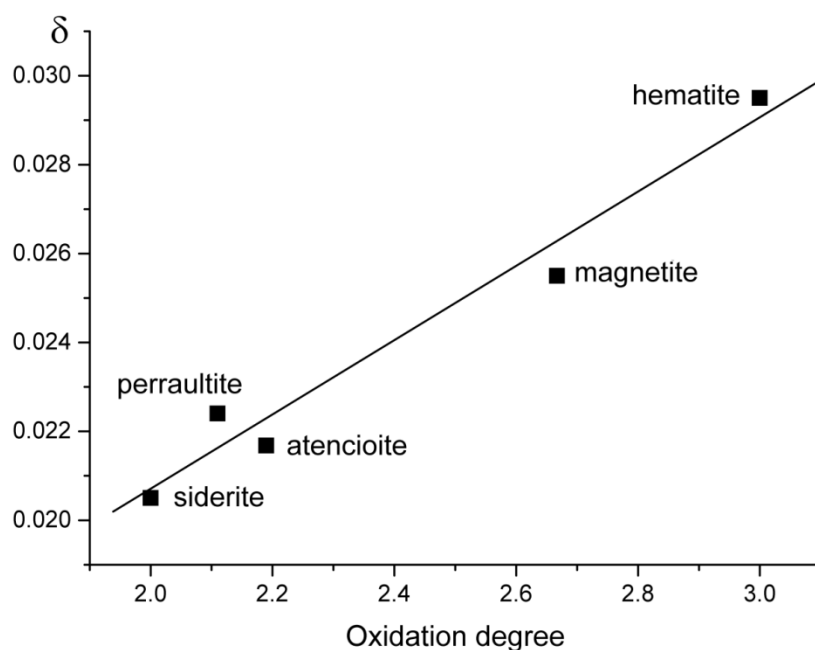


Fig. 1. Correlation between oxidation degree of iron in minerals and the ratio of intensities of the $\text{FeK}\beta_5$ and $\text{FeK}\beta_1$ lines in X-ray spectra.

Reflectance values for nioboixiolite-(Fe^{3+}) have been measured in air using an MSF-R (LOMO, St. Petersburg, Russia) microspectrophotometer. Silicon was used as a standard. The photometric aperture diameter was 0.3 mm, monochromator exit slit size 0.1 mm and spectral interval 6 nm.

Powder X-ray diffraction data were collected using a Rigaku R-Axis Rapid II diffractometer (image plate), $\text{CoK}\alpha$, 40 kV, 15 mA, rotating anode with the microfocus optics, Debye-Scherrer geometry, $r = 127.4$ mm, exposure 15 min. The raw powder XRD data were collected using program suite designed by Britvin *et al.* (2017). Calculated intensities were obtained by means of STOE WinXPOW v. 2.08 program suite based on the atomic coordinates and unit-cell parameters.

The raw powder XRD data were collected using the software of Britvin *et al.* (2017) and calculated intensities were obtained using software package STOE WinXPOW v.2.08 based on the atomic coordinates and unit-cell parameters.

The crystal structure was determined using single-crystal X-ray diffraction data and published elsewhere (Zubkova *et al.*, 2021). Crystal data, data collection information and structure

refinement details are given in Table 1. Experimental data were processed using the software package CrysAlisPro v. 1.171.39.46 (Rigaku, 2018). The crystal structure was determined by direct methods and refined using the set of programs SHELX (Sheldrick, 2015).

Results

Occurrence, General Appearance and Physical Properties

The new mineral occurs in cavernous nosean sanidine of the Laach Lake (Laacher See) volcano, Eifel region, Rhineland-Palatinate, Germany. The studied specimen was collected in the “In den Dellen” (Zieglowski) pumice quarry, 1.5 km NE of the town of Mendig (50°23'40" N, 7°17'12" E).

Associated minerals are sanidine, K-bearing albite, nosean, biotite, Nb-rich ilmenite, Ti-rich magnetite, hercynite, corundum, samarskite-(Y), ekebergite, and columbite-(Fe). Crystals of nioboixiolite-(Fe³⁺) and the above-listed associated oxide minerals occur on the walls of cavities of the host rock. Magnetite forms epitaxy on hercynite with a sharp border between the two spinel-group minerals. Nioboixiolite-(Fe³⁺) forms long prismatic to acicular crystals up to 0.03 × 0.06 × 1 mm elongated along the *c* axis and typically flattened on (100) (Fig. 2) and their epitaxial intergrowths with ilmenite (Fig. 3) as well as intermediate members of the samarskite–ekebergite series (Fig. 4). The main crystal forms are {100} and {010}. The subordinate (terminal) forms are {011} and {001}. Twinning is not observed.

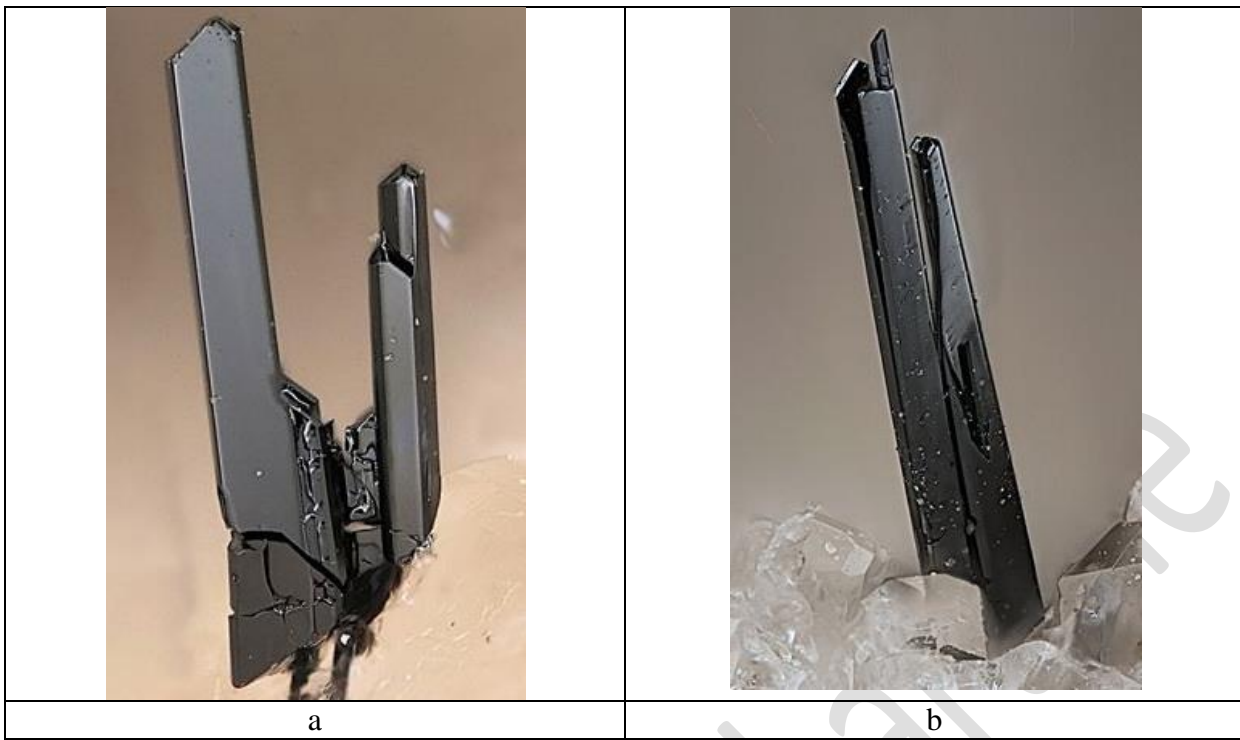


Fig. 2. Crystals of nioboixiolite-(Fe³⁺) on sanidine. FOV widths: 0.3 mm (a) and 0.5 mm (b).
Photos by V. Betz.



Fig. 3. Epitaxy of acicular crystals of nioboixiolite-(Fe³⁺) on a crystal of Nb-rich ilmenite overgrowing colourless sanidine. FOV width: 0.7 mm.

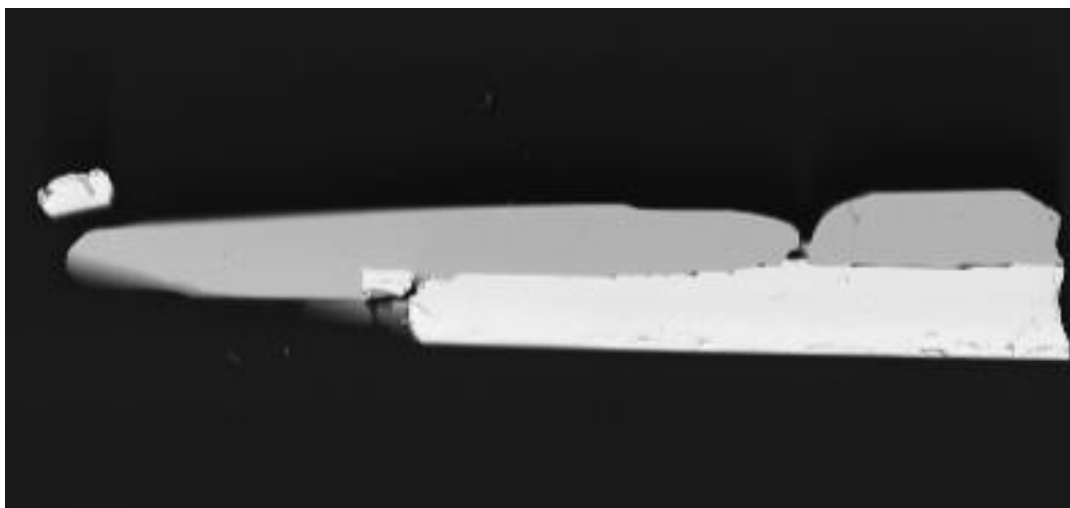


Fig. 4. Epitaxial overgrowth of nioboixiolite-(Fe³⁺) (darker crystal) on a zoned crystal consisting of two samarskite-series minerals, with samarskite-(Y) (inner) and ekebergite (outer) zones. SEM (BSE) image of a polished section. FOV width: 0.5 mm.

The colour and streak of nioboixiolite-(Fe³⁺) are black and the lustre is submetallic. Nioboixiolite-(Fe³⁺) is brittle. The mean hardness determined by micro-indentation (load 50 g) is 499 kg mm⁻² (range 433–560, *n* = 3) which corresponds to a Mohs' hardness of 5. The density of the new mineral could not be measured because of the absence of heavy liquids with *D* > 5 g cm⁻³ and scarcity of pure material to use volumetric method. Density calculated using the empirical formula and unit-cell volume refined from single-crystal XRD data is equal to 5.033 g·cm⁻³.

Raman spectroscopy

The Raman spectrum of nioboixiolite-(Fe³⁺) is given in Fig. 5. Taking into account force characteristics of cations, the bands at 860 and 385 cm⁻¹ can be assigned to stretching vibrations of (Nb,Ti)–O–(Nb,Ti) and (Nb,Ti)–O–Mn²⁺, respectively. The broad shoulder in the range of 500 – 600 cm⁻¹ may correspond to overlapping bands of stretching vibrations of (Nb,Ti)–O–M³⁺ and M³⁺–O–M³⁺

(M = Fe, Al, Cr). The bands at 166 and 274 cm^{-1} are tentatively assigned to bending vibrations and a mixed mode involving both stretching and bending internal coordinates, respectively.

The hump with the maximum at $\sim 2960 \text{ cm}^{-1}$ is due to luminescence from Fe^{3+} . No other bands are observed in the Raman spectrum of nioboixiolite-(Fe^{3+}) above 900 cm^{-1} which indicates the absence of H-, B- and C-bearing groups.

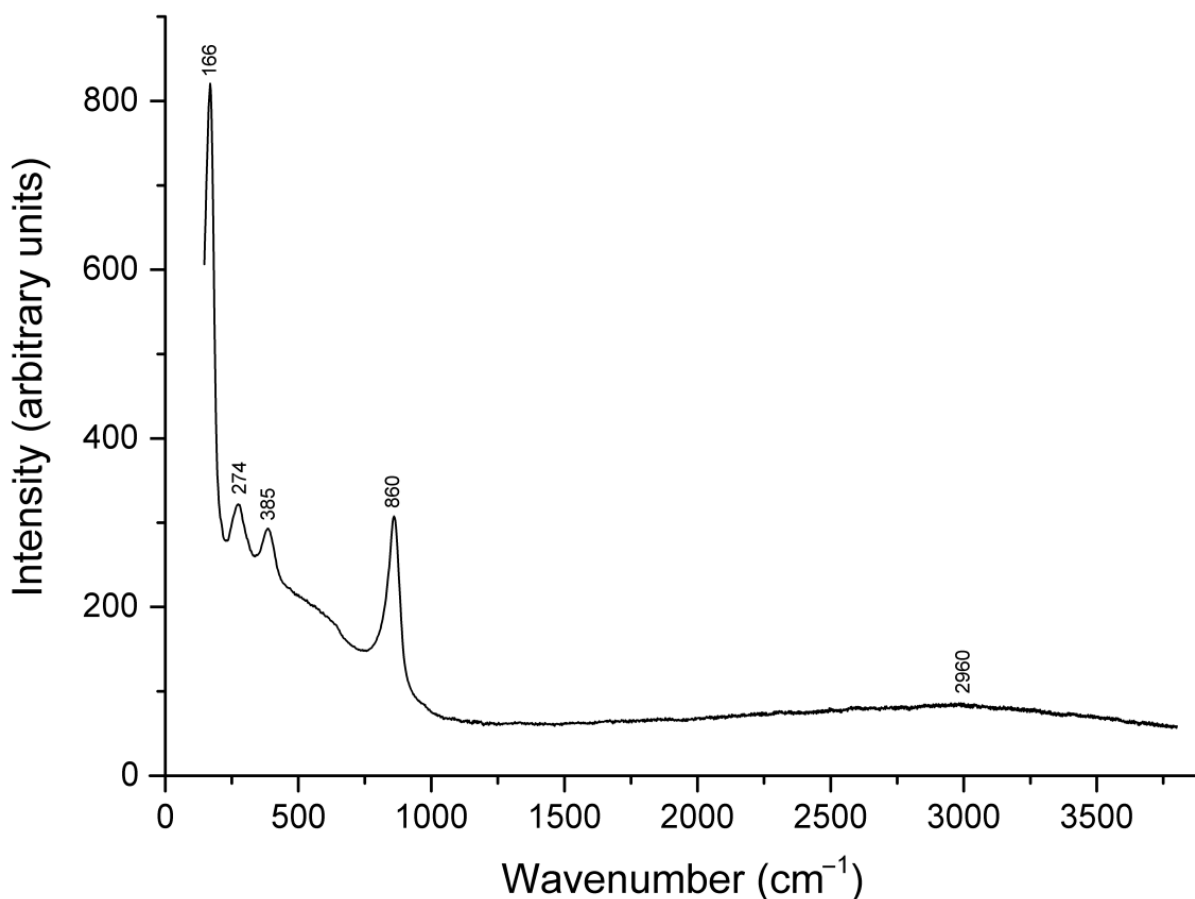


Fig. 5. The Raman spectrum of nioboixiolite-(Fe^{3+}).

Optical properties

In reflected light, nioboixiolite-(Fe^{3+}) is grey. Bireflectance is weak, $\Delta R = 1.6\%$ (589 nm). Pleochroism is not observed. Anisotropy is distinct, from light grey to grey. Internal reflections are strong, bright-orange.

The reflectance values ($R_{\text{max}}/R_{\text{min}}$) are given in the Table 2 and plotted in Fig. 6 in comparison with the published data for other members of the ixiolite group within the columbite supergroup.

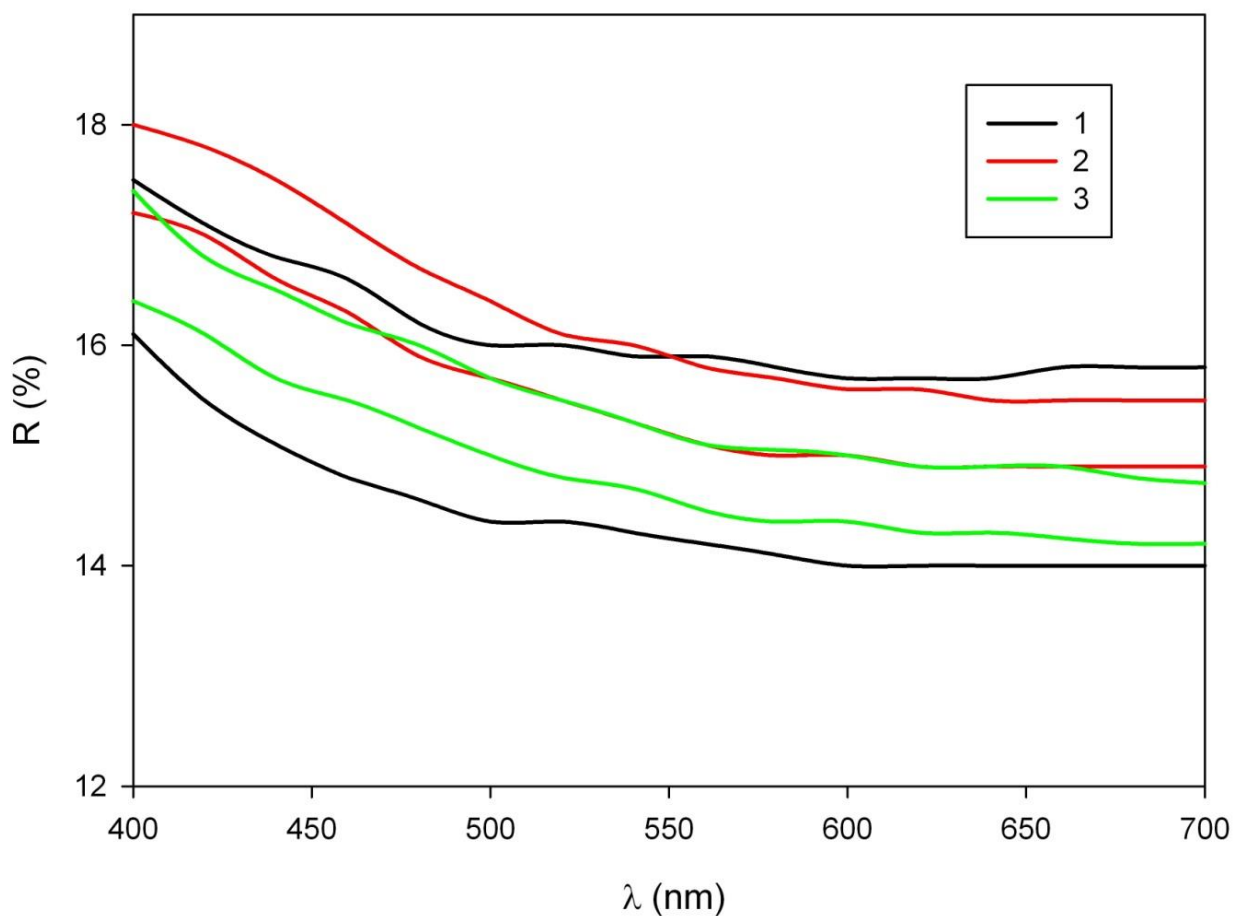


Fig. 6. The reflectance curves for nioboixiolite-(Fe³⁺) (1; this work), compared with published data for nioboixiolite-(Mn²⁺) from the Sosedka vein, Malkhan pegmatite field, Russia (2; after Chukanov *et al.*, 2023b) and ixiolite-(Mn²⁺) from Wodgina, Pilbara, Australia (3; after Criddle and Stanley, 1993).

Chemical Data

The analytical data are given in Table 3. H₂O was not measured because no bands corresponding to OH bearing groups were observed in the Raman spectrum. The crystal structure data confirmed the absence OH groups. The contents of elements with atomic numbers higher than that of carbon are below detection limits.

For nioboixiolite-(Fe³⁺), the $I(\text{Fe}K\beta_5)/I(\text{Fe}K\beta_5)$ ratio is equal to 0.02906 which corresponds to the oxidation degree of iron $\eta = 3.03 \pm 0.08$. Thus, all iron in nioboixiolite-(Fe³⁺) is trivalent.

The empirical formula calculated on 8 O atoms ($Z = 1$) is: $[(\text{Mg}_{0.04}\text{Mn}^{2+}_{0.20})_{\Sigma 0.24}(\text{Al}_{0.03}\text{Cr}_{0.04}\text{Fe}^{3+}_{1.01})_{\Sigma 1.08}(\text{Ti}_{1.11}\text{Zr}_{0.02})_{\Sigma 1.13}\text{Nb}_{1.55}]\text{O}_8$. In this formula calculated with only Fe^{3+} and only Mn^{2+} , the empirically obtained sum of cations is equal to 4.00. This is in a good agreement with trivalent state of iron determined from the X-ray spectrum.

In the empirical formula, the arrangement $[(\text{M}^{3+}_2\text{M}^{5+}_2)\text{O}^{2-}_8]$ (54%) is the dominant one, followed by arrangement $[\text{M}^{4+}_4\text{O}^{2-}_8]$ (28%) and arrangement $[(\text{M}^{2+}_{4/3}\text{M}^{5+}_{8/3})\text{O}^{2-}_8]$ (18%) (see Bosi *et al.*, 2019a,b). Thus, the ideal, end-member formula of nioboixiolite-(Fe^{3+}) is $(\text{Nb}_{0.5}\text{Fe}^{3+}_{0.5})\text{O}_2$ ($Z = 4$).

X-ray Diffraction and Crystal Structure

Powder X-ray diffraction data of nioboixiolite-(Fe^{3+}) are given in Table 4. The orthorhombic unit-cell parameters refined from the powder data are: $a = 4.652(1)$, $b = 5.625(1)$, $c = 5.015(1)$ Å; $V = 131.2(1)$ Å³.

The crystal structure of nioboixiolite-(Fe^{3+}) (Fig. 7) is the same as the structures of other ixiolite-group minerals. It is based upon zigzag-like chains of edge-shared MO_6 octahedra running along the c axis. Along the a axis, the chains are connected *via* common vertices of octahedra. All cations in the structure of nioboixiolite-(Fe^{3+}) are disordered and occur at the single M site whose occupancy was refined for Nb *vs.* Ti. The MO_6 octahedron is distorted, with two short $M\text{--O}$ distances [1.863(4) Å], two medium ones [1.988(4) Å] and two elongate bonds [2.207(4) Å] with average $\langle M\text{--O} \rangle = 2.019$ Å. Atom fractional coordinates, equivalent-isotropic displacement parameters and bond valence sums are presented in Table 5.

The refined number of electrons at the M site is 30.4, which is very close to 30.6 calculated from the empirical formula (the deviation is within experimental uncertainty).

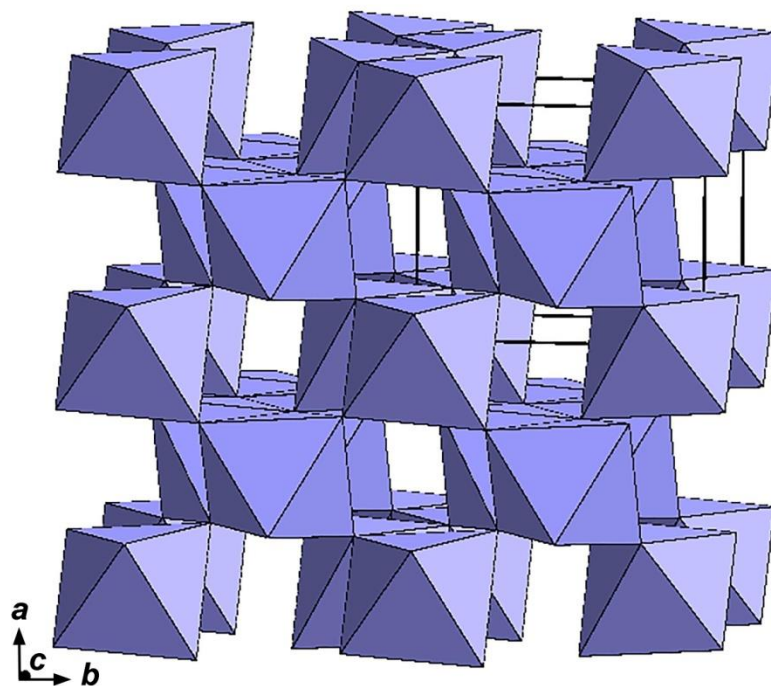


Fig. 7. The crystal structure of nioboixiolite-(Fe³⁺). The unit cell is outlined. The figure was drawn using Diamond Version 3.2k.

Discussion

Comparative data for nioboixiolite-(Fe³⁺) and chemically related columbite-supergroup minerals are given in Table 6. Nioboixiolite-(Fe³⁺) is dimorphous with rossovskyite, ideally Fe³⁺NbO₄, a mineral belonging to the wolframite group. The crystal structure of rossovskyite is a derivative of the ixiolite-type structure characterized by the ordering of the cations with lowering of the symmetry to monoclinic, space group *P2/c*. It can be represented as a sequence of two kinds of structurally identical, but chemically different, octahedral layers of parallel *zig-zag* chains alternating along the *a* axis (Konovalenko *et al.*, 2016).

A characteristic feature of the mineral studied in this work is the absence of tantalum in its composition, despite the fact that tantalum minerals of the ixiolite group are generally much more common than niobium members of this group. Apparently, the absence of tantalum in nioboixiolite-(Fe³⁺) is due to two reasons. On the one hand, niobium has a stronger affinity for structures with

highly distorted octahedra than tantalum. On the other hand, the absence of tantalum in nioboixiolite-(Fe³⁺) may be partly due to geochemical factors.

Most occurrences of ixiolite-group minerals, both Ta- and Nb-dominant, are related to granites and their derivatives. In general, feldspathoid rocks are characterized by extremely high Nb:Ta ratio (Parker and Fleischer, 1968) and tantalum-rich minerals are very rare in this formation. In particular, all Nb-bearing accessory minerals of this rock are significantly depleted in tantalum as compared to acidic igneous rocks and related pegmatites. In this reference, it is important to note that nosean syenite of the Laach Lake volcano is considered as a rock which is cogenetic with the phonolitic host magma and crystallized at temperatures below 700°C (Schmitt *et al.*, 2010).

Epitaxial intergrowths of nioboixiolite-(Fe³⁺) with ilmenite and minerals of the samarskite-(Y)–ekebergeite series are due to the topological similarity of chains of octahedra in their structures and, as a consequence, the near-commensurability of the parameters of their unit cells: for nioboixiolite-(Fe³⁺), $a \approx 4.66$ and $c \approx 5.02$ Å; for samarskite-(Y), $a/2 \approx 4.90$ and $c \approx 5.21$ Å; for ilmenite, $c/3 \approx 4.69$ and $a \approx 5.08$ Å.

Competing interests. The authors declare none.

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FIG. 1. Correlation between oxidation degree of iron in minerals and the ratio of intensities of the $\text{FeK}\beta_5$ and $\text{FeK}\beta_1$ lines in X-ray spectra.

FIG. 2. Crystals of nioboixiolite-(Fe^{3+}) on sanidinite. FOV widths: 0.3 mm (a) and 0.5 mm (b). Photos by V. Betz.

FIG. 3. Epitaxy of split acicular crystals of nioboixiolite-(Fe^{3+}) on a crystal of Nb-rich ilmenite overgrowing colourless sanidine. FOV width: 0.7 mm.

FIG. 4. Epitaxial overgrowth of nioboixiolite-(Fe^{3+}) (darker crystal) on a crystal of samarskite-series mineral with samarskite-(Y) (inner) and ekebergite (outer) zones. SEM (BSE) image of a polished section. FOV width: 0.5 mm.

FIG. 5. The Raman spectrum of nioboixiolite-(Fe^{3+}).

FIG. 6. The reflectance curves for nioboixiolite-(Fe^{3+}) (1; our data), compared with published data for nioboixiolite-(Mn^{2+}) from the Sosedka vein, Malkhan pegmatite field, Russia (2; Chukanov *et al.*, 2023b) and ixiolite-(Mn^{2+}) from Wodgina, Pilbara, Australia (3; Criddle and Stanley, 1993).

FIG. 7. The crystal structure of nioboixiolite-(Fe^{3+}). The unit cell is outlined. The figure was drawn using Diamond Version 3.2k.

Table 1. Crystal data, data collection information and crystal structure refinement details for nioboixiolite-(Fe³⁺).

Symmetry, space group, <i>Z</i>	Orthorhombic, <i>Pbcn</i> , 4
Unit cell parameters, Å	$a = 4.6578(6)$, $b = 5.6230(7)$, $c = 5.0182(5)$
V , Å ³	131.43(3)
Temperature, K	293(2)
Crystal sizes, mm	0.03 × 0.04 × 0.22
Diffractometer	Xcalibur S CCD
Radiation; λ , Å	MoK α ; 0.71073
θ_{\min}/\max , °	5.69 / 28.25
Ranges for data collection	$-6 \leq h \leq 6$, $-7 \leq k \leq 7$, $-6 \leq l \leq 6$
Reflections measured/independent	1547 / 163 ($R_{\text{int}} = 0.0411$)
Number of independent reflections with $I > 2\sigma(I)$	147
Refinement method	Full-matrix least-squares on F^2
Number of refined parameters	16
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0946P)^2 + 0.1606P]$
S	1.296
$R1$ [$I > 2\sigma(I)$], $wR2$ [all data]	0.0447, 0.1508
$\Delta\rho_{\max}/\min$, e/Å ³	2.197 / -2.548

Table 2. Reflectance data of nioboixiolite-(Fe³⁺).

λ (nm)	R_{\max}	R_{\min}		λ (nm)	R_{\max}	R_{\min}
400	17.5	16.1		560	15.9	14.2
420	17.1	15.5		580	15.8	14.1
440	16.8	15.1		589	15.7	14.1
460	16.6	14.8		600	15.7	14.0
470	16.4	14.7		620	15.7	14.0
480	16.2	14.6		640	15.7	14.0
500	16.0	14.4		650	15.8	14.0
520	16.0	14.4		660	15.8	14.0
540	15.9	14.3		680	15.8	14.0
546	15.9	14.3		700	15.8	14.0

Note: Data for COM standard wavelengths are given in bold.

Table 3. Chemical data for nioboixiolite-(Fe³⁺).

Constituent	Wt.%	Range	Standard deviation
MgO	0.41	0.28 – 0.55	0.10
MnO	3.52	3.21 – 3.88	0.24
Al ₂ O ₃	0.42	0.37 – 0.49	0.42
Cr ₂ O ₃	0.75	0.64 – 0.86	0.08
Fe ₂ O ₃	20.23	19.02 – 21.89	1.05
TiO ₂	22.26	20.97 – 23.75	0.99
ZrO ₂	0.76	0.50 – 0.98	0.21
Nb ₂ O ₅	51.82	49.16 – 54.49	1.91
Total	100.17		

Table 4. Powder X-ray diffraction data (d in Å) of nioboixiolite-(Fe³⁺).

I_{obs}	d_{obs}	I_{calc}^*	d_{calc}^{**}	$h k l$
29	3.586	29	3.587	110
100	2.917	100	2.918	111
14	2.812	12	2.812	020
18	2.503	12	2.509	002
10	2.452	13	2.453	021
7	2.329	5	2.329	200
9	2.207	4	2.209	102
18	2.170	9	2.170	121
15	2.056	8	2.056	112
13	1.876	6	1.872	022
6	1.794	4	1.794	220
22	1.738	13	1.739	130
11	1.707	17	1.707	202
26	1.689	22	1.689	221
15	1.515	13	1.516	113
15	1.435	9, 11	1.438, 1.434	023, 311
15	1.431	12	1.429	132
3	1.356	5	1.354	041
4	1.284	2	1.285	312
4	1.221	2	1.223	223
5	1.194	3	1.196	330
5	1.170	7	1.170	241
5	1.163	3	1.164	400
4	1.115	4	1.115	313
6	1.078	7	1.079	332

* For the calculated pattern, only reflections with intensities ≥ 1 are given.

** For the unit-cell parameters obtained from single-crystal data.

Table 5. Fractional coordinates, equivalent-isotropic displacement parameters (U_{eq} , in \AA^2) of atoms and bond valence sums (BVS) in the structure of nioboixiolite-(Fe³⁺).

Site	x/a	y/b	z/c	U_{eq}	BVS*
<i>M</i>	0	0.17575(17)	1/4	0.0119(8)	3.98
O	0.2709(7)	0.3671(7)	0.4191(9)	0.0152(17)	1.99

* BVS were calculated using the parameters from Gagné and Hawthorne (2015) for the *M* site with the occupancy Nb_{0.5}Fe³⁺_{0.5}.

Table 6. Comparative data for nioboixiolite-(Fe³⁺) and related columbite-supergruop minerals

Mineral	Nioboixiolite-(Fe ³⁺)	Nioboixiolite-(Mn ²⁺)	Nioboixiolite-(□)	Dmitryvarlamovite	Rossovskyite
Ideal formula	(Nb _{0.5} Fe ³⁺ _{0.5})O ₂	(Mn ²⁺ _{1/3} Nb _{2/3})O ₂	(Nb _{0.8} □ _{0.2})O ₂	Ti ₂ (Fe ³⁺ Nb)O ₈	Fe ³⁺ NbO ₄
Mineral group	Ixiolite	Ixiolite	Ixiolite	Wolframite	Wolframite
Crystal system	Orthorhombic	Orthorhombic	Orthorhombic	Orthorhombic	Monoclinic
Space group	<i>Pbcn</i>	<i>Pbcn</i>	<i>Pbcn</i>	<i>P2₁2₁2</i>	<i>P2/c</i>
<i>a</i> , \AA	4.6578(6)	4.7559	4.7071	4.9825(6)	4.668
<i>b</i> , \AA	5.6230	5.7318	5.7097	4.6268(4)	5.659
<i>c</i> , \AA	5.0182(5)	5.1344	5.1111	5.5952(6)	5.061
β , °	90	90	90	90	90.21
<i>V</i> , \AA^3	131.43	139.97	137.37	128.98	133.70
<i>Z</i>	4	4	4	1	2
Strongest reflections of the powder X-ray diffraction pattern:	3.586 (29) 2.917 (100) 2.503 (18) 2.170 (18) 2.056 (15) 1.738 (22) 1.689 (26) 1.515 (15) 1.435 (15) 1.431 (15)	3.662 (29) 2.984 (100) 2.505 (21) 1.775 (21) 1.748 (28) 1.726 (35) 1.553 (20) 1.473 (19) 1.463 (30)	3.662 (20) 2.975 (100) 2.566 (10) 2.501 (20) 2.096 (10) 1.770 (20) 1.718 (15) 1.458 (20)	3.58 (40) 2.911 (100) 2.809 (40) 2.497 (38) 2.447 (29) 1.7882 (26) 1.7363 (32) 1.7047 (39)	3.604 (49) 2.938 (100) 2.534 (23) 2.476 (29) 2.337 (27) 1.718 (26) 1.698 (31) 1.440 (21)
Density, g cm ⁻³	5.033 (calc.)	5.803 (calc.)	6.05 (calc.)	4.79 (calc.)	6.06 (meas.) 6.30 (calc.)
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