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Nioboixiolite-(□),$(Nb_{0.8}\square_{0.2})^{4+}O_2$, a New Mineral Species from the Bayan Obo World-Class REE-Fe-Nb Deposit, Inner Mongolia, China

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Abstract: Nioboixiolite-(□) is a new mineral found in a carbonatite sill from the Bayan Obo mine, Baotou City, Inner Mongolia, China. It occurs as anhedral to subhedral grains (100 to 500 μm in diameter) that are disseminated in carbonatite rock composed of dolomite, calcite, magnetite, apatite, biotite, actionlike, zircon, and columbite-(Fe). Most of these grains are highly serrated, with numerous inclusions of columbite-(Fe). The mineral is gray to deep black in color; is opaque, with a semi-metallic luster; has a black streak; and is brittle, with an uneven conchoidal splintery. The Mohs hardness is 6–6½, and the calculated density is 6.05 g/cm^3. The reflection color is gray with a blue tone, and there is no double reflection color. The measured reflectivity of nioboixiolite-(□) is about 10.6%~12.1%, close to that of ixiolite (11%–13%). Nioboixiolite-(□) is non-fluorescent under 254 nm (short-wave) and 366 nm (long-wave) ultraviolet light. The average chemical analysis results (wt.%) of twelve electron microprobe analyses are F 0.01, MnO 0.12, MgO 0.15, BaO 0.62, PbO 0.91, SrO 1.49, CaO 2.76, Al_2O_3 0.01, $TREE_2O_3$ 1.58, Fe_2O_3 3.57, ThO_2 0.11, SiO_2 1.69, TiO_2 3.68, Ta_2O_5 13.95, Nb_2O_5 47.04, and UO_3 21.56, with a total of 99.25. The simplified formula is $[Nb^{5+}, Ta^{5+}, Ti^{4+}, Fe^{3+}, \square,]O_2$. X-ray diffraction data show that nioboixiolite-(□) is orthorhombic, belonging to the space group *Pbcn* (#60). The refined unit cell parameters are a = 4.7071(5) Å, b = 5.7097(7) Å, c = 5.1111(6) Å, V = 138.31(3), and β = 90(1) °Å^3 with Z = 4. In the crystal structure of nioboixiolite-(□), all cations occupy a single M1 site. In these minerals, edge-sharing M_1O_6 octahedra form chains along the ***c*** direction. In this direction, the chains are connected with each other via common vertices of the octahedra. The strongest measured X-ray powder diffraction lines are [d in Å, (I/I0), (hkl)]: 3.662(20) (110), 2.975(100) (111), 2.501(20) (021), 1.770(20) (122), 1.458(20) (023). A type specimen was deposited in the Geological Museum of China with catalogue number M16118, No. 15, Yangrou Hutong, Xisi, Beijing 100031, People's Republic of China.

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1. Introduction

According to the nomenclature of the columbite-supergroup minerals [1] approved by the Commission on New Minerals, Nomenclature and Classification of the International Mineralogical Association (IMA-CNMNC), the columbite supergroup comprises five mineral groups (ixiolite, wolframite, samarskite, columbite, and wodginite) and one ungrouped species. The ixiolite group structure is considered an aristotype with the space group *Pbcn*, the smallest unit cell volume, and the basic vectors a_0, b_0, and c_0. The other mineral groups are distinguished on the basis of the multiplying of the ixiolite-type unit cell. Ixiolite was first described by Nordenskiöld (1857) as a tantalumoxide, with subordinate Fe and Mn and minor Sn. The Nb-dominant analogue of ixiolite (with Nb > Ta) has been known for a long time [2–5].

Although there is only one cationic M1 site in the ixiolite-type structure, the ixiolite and its Nb-dominant analogue cannot be written with a single cationic component. The dominant charge-compensating cations (DCCC) (either a lower-valency cation or vacancy) should be taken into account when distinguishing between different kinds of minerals: the end-member formula will depend on the dominant cation within the dominant valence state of the charge-compensating cation [1]. According to this procedure, the well-known mineral ixiolite [6,7] was given the new species name ixiolite-(Mn^{2+}) and the charge-balanced end-member formula $(Ta_{2/3}Mn_{1/3}{}^{2+})O_2$. For the Nb-dominant analogues of ixiolite, there are different schemes of charge-balancing known from numerous localities [2]. The nioboixiolite-(Mn^{2+}) was found in the Malkhan pegmatite field, Transbaikal Region, Russia [2]. The new mineral species nioboixiolite-(□), ideally $(Nb_{0.8}\square_{0.2})^{4+}O_2$, described in this article is the other one. Nioboixiolite-(□) is a Nb-dominant analogue of ixiolite and isostructural with nioboixiolite-(Mn^{2+}), but the charge-balanced end-member is a vacancy, so they are two different minerals. Nioboixiolite-(□) is also isostructural with other members of the ixiolite group, scrutinyite α-PbO_2 [8], srilankite, $(Ti,Zr)O_2$ [3,9], and seifertite, SiO_2 [10], with different chemical compositions. Thus, nioboixiolite-(□) is a niobium analogue of all these minerals belonging to the α-PbO_2 structure type, similar to nioboixiolite-(Mn^{2+}) [2]. The new mineral nioboixiolite-(□) and its name were approved by the IMA-CNMNC (IMA No. 2021-02a). A type specimen was deposited in the Geological Museum of China with the catalogue number M16118.

2. Analytical Methods

Polished thin sections were prepared for investigation using optical microscopy, scanning electron microscopy, and Raman spectroscopy. Mineral grains were separated using a gravitational technique, handpicked under a binocular microscope, and cast in an epoxy mount, then polished to about half of the average grain thickness for composition analysis and age dating.

2.1. Chemical Composition Analysis

Quantitative major and trace elemental analyses of nioboixiolite-(□) were carried out at the Institute of Mineral Resources, Chinese Academy of Geological Sciences, using a JXA-iHP200F electron microprobe (Japan Electron Optics Laboratory, Tokyo, Japan). The analysis was performed with an accelerating voltage of 15 kV and a beam current of 20 nA in the spot mode, with the spot size being less than 5 μm. Twelve analyses (spots) were conducted on a single nioboixiolite-(□) crystal grain, which was also used for the structural study with single-crystal X-ray diffraction. Natural minerals and synthetic materials were used as standard samples, and all the standard samples were tested for homogeneity before their utilization for quantitative analysis. Matrix corrections were carried out using the ZAF correction program supplied by the manufacturer.

2.2. Crystal Structural Analysis

Single-crystal X-ray diffraction was carried out at the Crystal Structure Laboratory Science Research Institute, China University Geosciences, Beijing, using a Rigaku Oxford Diffraction XtaLABPRO-007HF (Rigaku, Tokyo, Japan) rotating anode microfocus X-ray source (1.2 kW Mo$K\alpha\lambda$ = 0.71073 Å) and a hybrid pixel array detector single-crystal diffractometer. The experimental conditions were 50 kV and 24 mA, and the exposure time was 15 s per frame, with a single crystal fragment of 110 μm × 70 μm × 50 μm in size.

X-ray powder diffraction data were also collected using the same equipment and analytical conditions with a crystal rotation method.

2.3. Infrared Absorption Spectroscopy Analysis

An infrared absorption spectroscopy analysis was conducted in attenuated total reflection (ATR) mode at the Institute of Mineral Resources, Chinese Academy of Geological Sciences (CAGS), Beijing, China, using a VERTEX 70 infrared spectrometer (Bruker, Karlsruhe, Germany) equipped with a microscope. The wave number range was set from 4000 cm^{-1} to 400 cm^{-1}, with a resolution of 8 cm^{-1}. Each sample was scanned 64 times and averaged to improve the signal-to-noise ratio. The analysis was performed at room temperature, with samples directly in contact with the diamond ATR crystal surface, requiring no additional sample preparation. To prevent interference from environmental water vapor and CO_2, dry air was used to purge the instrument's sample chamber during measurements. OPUS (version: 7.2.139.1294) software was used to collect and process the infrared spectra of the samples.

2.4. Raman Spectroscopy Analysis

Raman spectroscopy was obtained on a fragment of nioboixiolite-(□) using a LabRAM Odyssey Raman spectrometer (HORIBA Scientific, Paris, France) equipped with a 532 nm excitation laser, at the Institute of Mineral Resources, Chinese Academy of Geological Sciences (CAGS), Beijing, China. The analysis was operated at a power of 48.4 mW, with integration times of 10~20 s. Raman spectra were collected with a 50× objective to provide a spatial resolution of 0.2 cm^{-1}. The spectra were fitted using the fast Fourier transform method after background subtraction with a polynomial function. The assignment of Raman bands to vibration modes was made based on published data.

2.5. Reflectance Test Analysis

The Reflectance of nioboixiolite-(□) was tested using UV-VIS-NIR Microspectrophotometer (CRAIC Technologies, Inc., San Dimas, CA, USA), at the State Key Laboratory of Radiation Medicine and Protection, School for Radiological and Interdisciplinary Sciences, Soochow University, Suzhou, Jiangsu, China. Test condition: Time 1 = 214 ms: Average 1 = 5: Objective = 10× UV: Aperture = 4.

2.6. X-Ray Photoelectron Spectroscopy (XPS) Analysis

A fragment of nioboixiolite-(□) was also chosen for the XPS analysis to confirm the valency of Fe and U. The analysis was conducted with a PHI 5000 Versa Probe III (ULVAC-PHI, Maozaki, Japan) equipped with a monochromatic Al Kα X-ray source with a beam size of 100 um at the PHI China Analytical Laboratory, Nanjing. Charge compensation was achieved with dual beam charge neutralization and the binding energy was corrected by setting the binding energy of the hydrocarbon C 1 s feature to 284.8 eV.

3. Results

3.1. Occurrence and Associated Minerals

Nioboixiolite-(□) was found by the first author during field work in a carbonatite sill from the Bayan Obo deposit, Inner Mongolia, North China (41°47′25″ N, 109°50′00″ E, Figure 1A). The Bayan Obo deposit is now mined in three open pits, the East, Main, and West, from east to west (Figure 1B). A group of concealed carbonatite sills was discovered at about 1.5 km southwest of the West Mine, covering an area of about 7000 m in length and 150 m in width (Figure 1C), during the drilling exploration for iron resource. These carbonatite sills are discontinuous and are covered by the Cretaceous Guyang Formation as revealed by the drilling project [11].

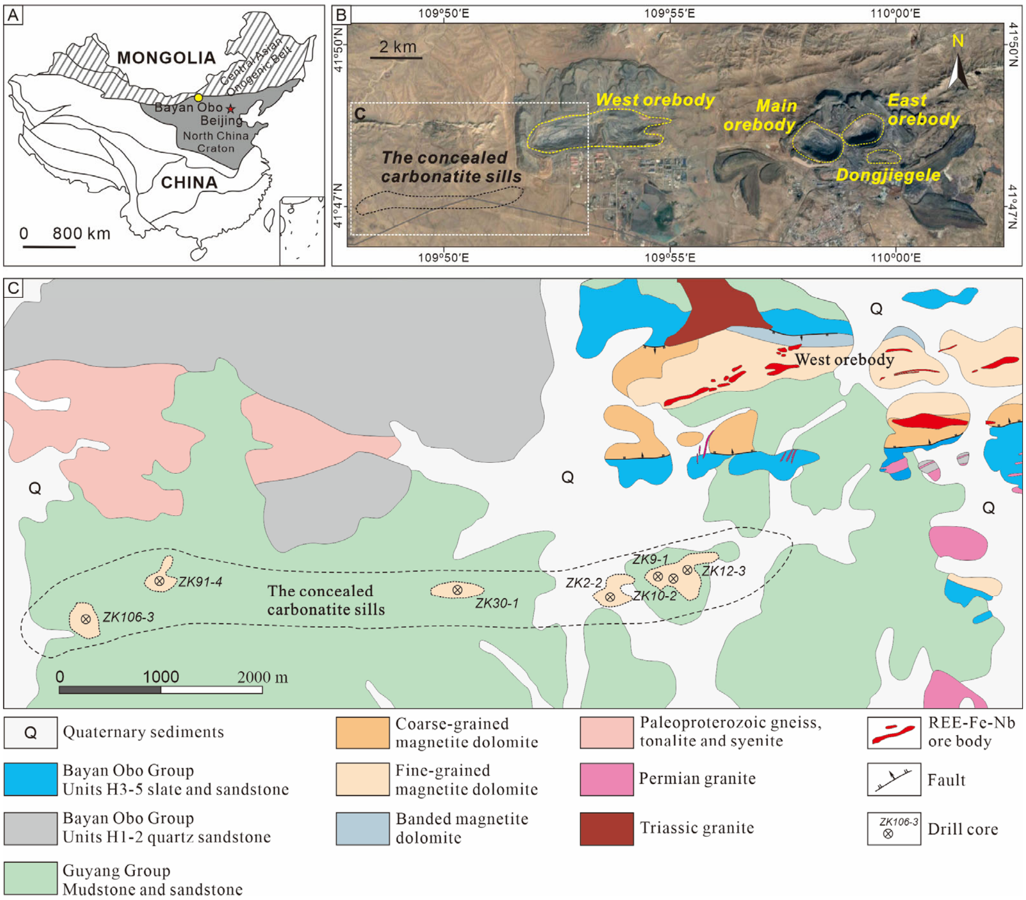

Figure 1. (**A**) Simplified tectonic subdivision of China, showing the location of Bayan Obo; (**B**) arial image showing the locations of the main orebodies and the concealed carbonatite sills in the Bayan Obo area; (**C**) geological sketch of the study area, showing the locations of drill cores and concealed carbonatite sills.

Nioboixiolite-(□) was found in a fine-grained, gray/white dolomite-type carbonatite in drill core ZK106-3 (Figure 1C). Lithologically, the carbonatite rocks can be further divided into dolomite carbonatite and calcite carbonatite. The dominant minerals in these carbonatites are dolomite (and/or calcite, >90%) and magnetite, while minor components (<10%) including pyrite, apatite, biotite, and zircon, as well as Nb- and REE-bearing minerals (e.g., columbite-(Fe)), are also present.

3.2. Optical, Morphological and Physical Properties of Nioboixiolite-(□)

Nioboixiolite-(□) is black in color and occurs as disseminated grains with diameters varying from less than 100 to 500 μm in the dolomite-type carbonatite (Figure 2A,B). Most of them are sphenoidal in shape and highly serrated (Figure 2B), while others are anhedral (Figure 2C). It is noteworthy that nioboixiolite-(□) generally shows a typical petrographic feature of replacing columbite-(Fe) (Figure 2C), while numerous inclusions of columbite-(Fe) are also observed within nioboixiolite-(□) grains (Figure 2D). The refractive index of nioboixiolite-(□) could not be observed due to its opaque nature under microscope, while its reflection color is gray with a blue tone and the mineral is non-pleochroic. The reflectance of nioboixiolite-(□) is of grade V, with measured reflectivity of 10.6%~12.1%, close to that of ixiolite (11%~13%). The streak, luster, and hardness (Mohs) of nioboixiolite-(□) are black, semi-metallic to opaque, and 6–6½, respectively. The calculated density is 6.05 g·cm^{-3} based on the empirical formula and single-crystal X-ray diffraction data, while the tenacity is brittle according to the SEM image. Nioboixiolite-(□) is non-fluorescent under 254 nm (short-wave) and 366 nm (long-wave) ultraviolet light. A type specimen was deposited in the Geological Museum of China with the catalogue number M16118, No. 15, Yangrou Hutong, Xisi, Beijing 100031, China.

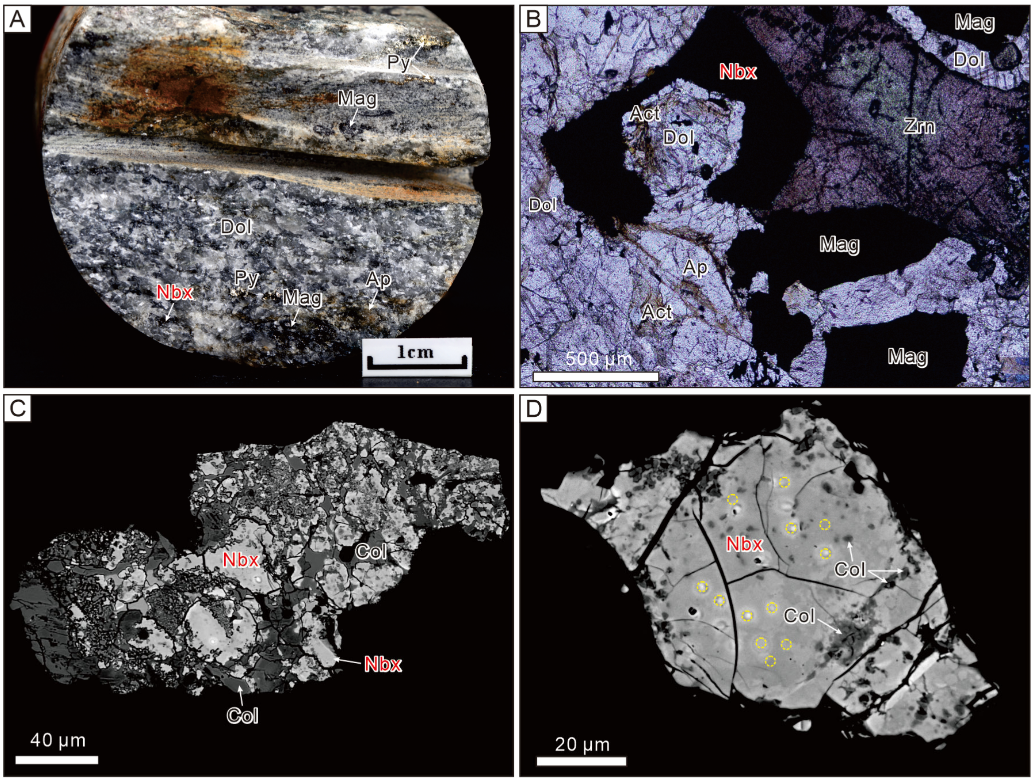

Figure 2. Representative photographs and photomicrographs of samples from the Bayan Obo REE-Fe-Nb deposit: (**A**) picture of the fine-grained dolomite-type carbonatite which contains nioboixiolite-(□); (**B**) photomicrograph (transmitted-light) showing the dominant minerals within the dolomite-type carbonatite; (**C**) backscattered electron (BSE) image of separated nioboixiolite-(□) grain showing the columbite-(Fe) being replaced by nioboixiolite-(□); (**D**) BSE image of a single nioboixiolite-(□) crystal, the yellow dotted circles showing the areas for EPMA analysis. Abbreviations: Mag = magnetite, Py = pyrite, Dol = dolomite, Ap = apatite, Nbx = nioboixiolite-(□), Zrn = zircon, Act = actinolite, Col = columbite-(Fe).

3.3. Infrared Absorption Spectroscopy

The IR spectrum of nioboixiolite-(□) (Figure 3) contains a strong band at 590 cm^{-1} (with secondary bands at 500 and 600 cm^{-1}) corresponding to cation–oxygen stretching vibrations and weak bands at 538, 527 and 546 cm^{-1} assigned as overtones. The characteristic bands of O–H and O–C bonds are absent in the spectrum.

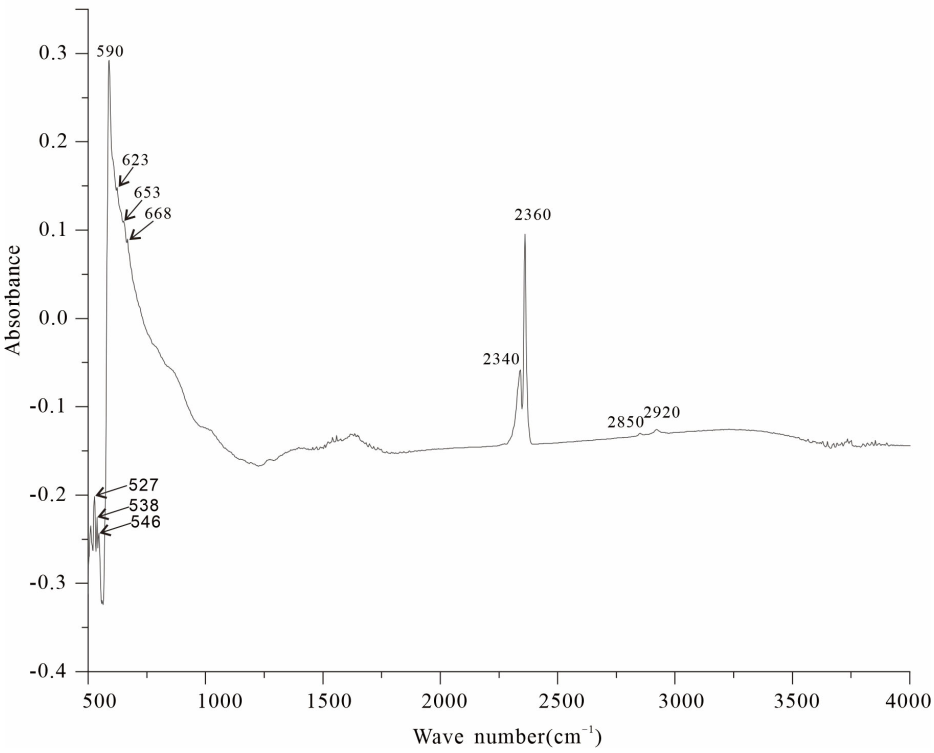

Figure 3. IR absorption spectrum of nioboixiolite-(□).

3.4. Raman Spectroscopy

The strongest Raman bands of nioboixiolite-(□) are at 266.18 cm^{-1}, 461.56 cm^{-1}, 720.66 cm^{-1}, and 790.68 cm^{-1}, with corresponding FWHM values of 69.19 cm^{-1}, 55.69 cm^{-1}, 68.69 cm^{-1}, and 60.57 cm^{-1}, respectively. A representative Raman spectrum of nioboixiolite-(□) is shown in Figure 4, with information on the Raman characteristic bands (band position and FWHM) provided in Table 1.

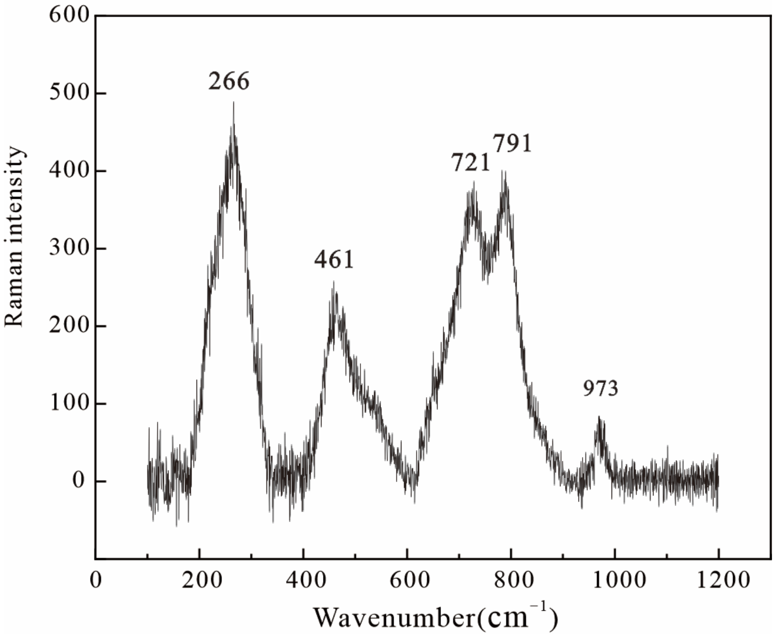

Figure 4. Raman spectrum of nioboixiolite-(□).

Table 1. Representative positions and FWHM values of the characteristic Raman bands of nioboixiolite-(☐).

Peak	Type	Amplitude	Center	FWHM	Asym50	FW Base	Asym10
1	Gauss + Lor Amp	418.03	266.179	69.19	1	138.50	1
2	Gauss + Lor Amp	193.65	461.561	55.69	1	112.75	1
3	Gauss + Lor Amp	293.17	720.66	68.69	1	137.50	1
4	Gauss + Lor Amp	344.33	790.68	60.57	1	188.18	1

3.5. Chemical Composition

The analytical data of nioboixiolite-(☐) are given in Table 2. The contents of other elements with atomic numbers of >8 were below the detection limits. As shown in Table 2, nioboixiolite-(☐) displays narrow ranges of Nb_2O_5 and UO_3 contents of 43.86~51.80 wt.% and 19.12~21.56 wt.%, respectively, and variable contents of Ta_2O_5 (10.26~15.22 wt.%), TiO_2 (3.05~4.91 wt.%), Fe_2O_3 (2.41~4.77 wt.%), CaO (2.22~3.44 wt.%), and SrO (1.11~2.16 wt.%). Other components, such as SiO_2, BaO, and Ce_2O_3, are relatively low and more variable in their contents, ranging from 0.80 to 3.86 wt.%, from 0.07 to 1.34 wt.%, and from 0.29 to 1.13 wt.%, respectively.

Table 2. Electron microprobe analysis results for nioboixiolite-(☐).

Constituent	Wt.% *	Range	Stand. Dev.	Probe Standard
Nb_2O_5	47.04	43.86–51.80	2.09	$KNbO_3$
Ta_2O_5	13.95	10.26–15.22	1.25	$LiTaO_3$
UO_3 *	21.56	19.12–21.56	1.32	thorianite
TiO_2	3.68	3.05–4.91	0.53	rutile
Fe_2O_3 *	3.57	2.41–4.77	0.81	hematite
CaO	2.76	2.22–3.44	0.37	wollastonite
MgO	0.15	0.0–0.43	0.13	forsterite
SiO_2	1.69	0.80–3.86	0.96	Jade
SrO	1.49	1.11–2.16	0.31	$SrSO_4$
BaO	0.62	0.07–1.34	0.46	$BaSO_4$
La_2O_3	0.08	0.00–0.14	0.04	LaP_5O_{14}
Ce_2O_3	0.68	0.29–1.13	0.23	CeP_5O_{14}
Pr_2O_3	0.10	0.00–0.22	0.07	PrP_5O_{14}
Nd_2O_3	0.25	0.00–0.37	0.12	NdP_5O_{14}
Sm_2O_3	0.04	0.00–0.09	0.04	SmP_5O_{14}
Eu_2O_3	0.02	0.00–0.11	0.04	EuP_5O_{14}
Gd_2O_3	0.06	0.00–0.15	0.05	GdP_5O_{14}
Tb_2O_3	0.13	0.00–0.36	0.14	$Tb_3Ga_5O_{12}$
Dy_2O_3	0.05	0.00–0.17	0.06	DyP_5O_{14}
Ho_2O_3	0.04	0.00–0.18	0.06	HoP_5O_{14}
Er_2O_3	0.02	0.00–0.11	0.03	ErP_5O_{14}
Tm_2O_3	0.02	0.00–0.14	0.04	$Tm\ P_5O_{14}$
Yb_2O_3	0.04	0.00–0.29	0.08	$Yb\ P_5O_{14}$

Table 2. *Cont.*

Constituent	Wt.% *	Range	Stand. Dev.	Probe Standard
Lu2O3	0.03	0.00–0.15	0.05	$LuSiO_5$
Y_2O_3	0.02	0.00–0.13	0.04	$Y P_5O_{14}$
MnO	0.12	0.00–0.29	0.08	$MnTiO_3$
PbO	0.91	0.76–1.06	0.08	$PbCr_2O_4$
ThO_2	0.11	0.07–0.16	0.03	thorianite
Al_2O_3	0.01	0.00–0.03	0.01	jadeite
F	0.01	0–0.09	0.02	phlogopite
Total	99.25	98.72–99.93	0.38	

* Ferric iron and hexavalent uranium in nioboixiolite-(□) were inferred by means of XPS.

The empirical formula calculated based on 8 O *apfu* for nioboixiolite-(□) is $[Nb_{2.36}Ta_{0.42}Ti_{0.31}Fe_{0.30}\square_{0.62}]_4O_8$, while the simplified formula is $[Nb^{5+}, Ta^{5+}, Ti^{4+}, Fe^{3+}, \square,]O_2$, and the end-member ideal formula is $(Nb_{0.8}\square_{0.2})^{4+}O_2$, which requires Nb_2O_5 100.00 wt.%, for a total of 100.00 wt.%. The valences of U and Fe were inferred from the XPS spectra (Figure 5) and the standard binding energies of U^{6+} (380.31 ± 0.47 eV, [12]) and Fe^{3+} (710.9 eV, [13]), which are likely to be hexavalent and trivalent for nioboixiolite-(□), respectively.

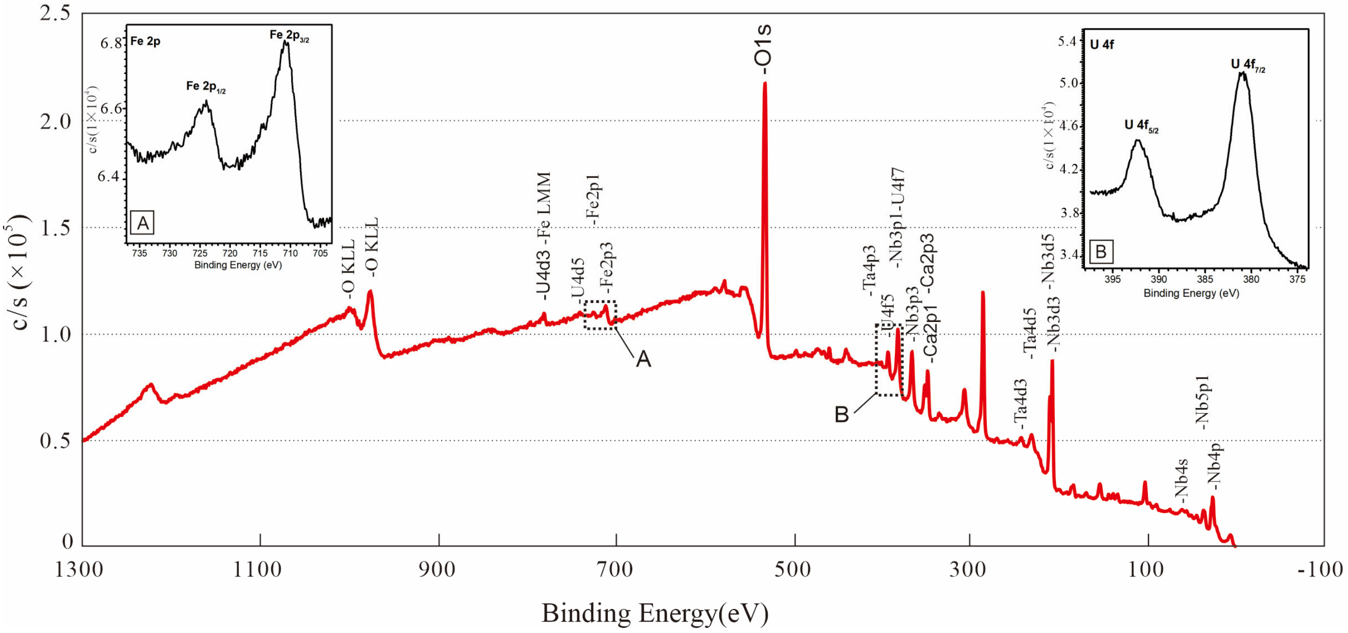

Figure 5. XPS spectra of iron (**A**) and uranium (**B**) in nioboixiolite-(□) obtained with Al Kα X-ray source (1486.6 eV).

3.6. Crystal Structure

The X-ray powder diffraction data for nioboixiolite-(□) are given in Table 3. The X-ray powder diffraction pattern of nioboixiolite-(□) (MoKα) is shown in Figure 6. The strongest measured X-ray powder diffraction lines were [d in Å, (I/I0), (hkl)]: 3.662(20) (110), 2.975(100) (111), 2.501(20) (021), 1.770(20) (122), and 1.458(20) (023). The structure refinement details for nioboixiolite-(□) are presented in Table 4. Nioboixiolite-(□) is orthorhombic; its unit cell parameters were obtained from both single-crystal and X-ray powder data, giving *a* = 4.7211(10) Å, *b* = 5.7225(12) Å, *c* = 5.1192(12) Å, *V* = 138.31(9) $Å_3$, and an *a*/*b*/*c* ratio of 1:1.212997:1.085828.

Table 3. X-ray powder diffraction data for nioboixiolite-(□).

h	*k*	*l*	*d*(obs)	*d*(calc)	I/I_0
1	1	0	3.6621	3.6417	20
1	1	1	2.9746	2.9675	100
0	2	0	2.8603	2.8613	4
0	0	2	2.566	2.5596	10
0	2	1	2.5008	2.4976	20
2	0	0	2.3637	2.3606	2
1	0	2	2.2605	2.2502	2
1	2	1	2.2104	2.2077	6
1	1	2	2.0958	2.0941	10
0	2	2	1.9075	1.9077	6
2	2	0	1.8234	1.8209	2
1	2	2	1.7702	1.7687	20
2	2	1	1.7177	1.7156	15
1	1	3	1.5453	1.5452	10
0	2	3	1.4581	1.4656	20
0	4	1	1.3793	1.3778	10
3	1	2	1.3058	1.3053	1
0	4	2	1.2465	1.2488	2
3	3	0	1.2108	1.2139	2
2	4	1	1.19	1.19	2
4	1	1	1.1267	1.1276	2
0	4	3	1.0973	1.0963	8
1	3	4	1.0365	1.0368	2
2	4	3	0.9952	0.9943	2

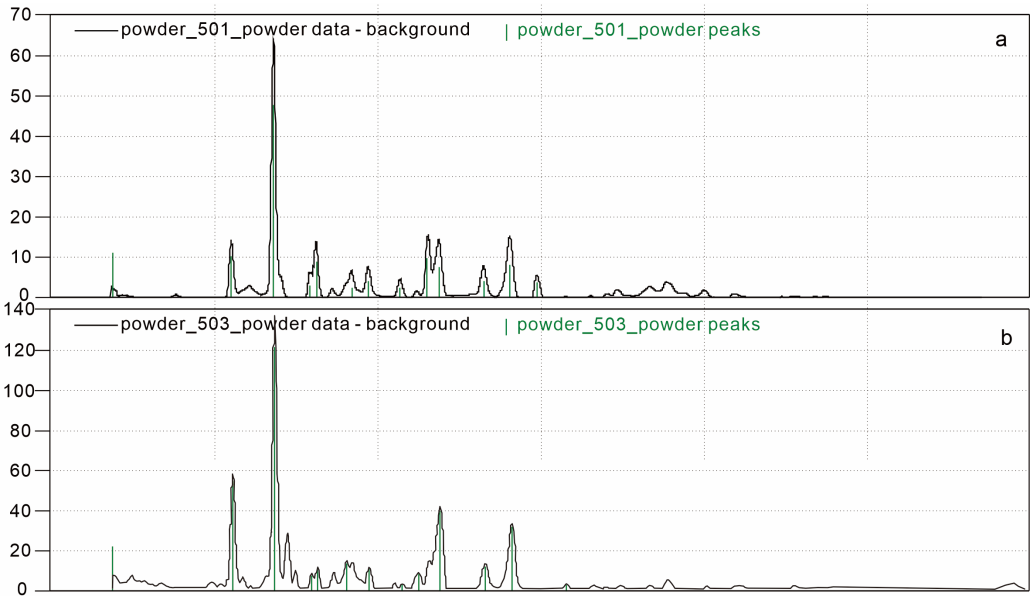

Figure 6. X-ray powder diffraction pattern of nioboixiolite-(□) (Mo$K\alpha$) (**a**) and columbite-(Fe) (**b**).

The crystal structure of nioboixiolite-(□) was determined and further refined with the program SHELX [14,15]; its atom coordinates, displacement parameters, anisotropic displacement parameters, and bond distances are provided in Table 5. The structure was solved in the space group *Pbcn*(#60), and the final refinement cycles converged to $R1 = 0.03$, w$R2 = 0.11$, and GooF = 0.94 for all data. The crystal structure of nioboixiolite-(□) is shown in Figure 7 and is identical to that of ixiolite [2].

Table 4. Data collection and structure refinement details for nioboixiolite-(☐).

Structural formula	$Nb_{0.88}O_2$	θ range for data collection/ °	5.615–29.335°
Formula weight	124.91	Index ranges	$-6 \leq h \leq 6$, $-7 \leq k \leq 7$, $-6 \leq l \leq 6$
Crystal system	orthorhombic	Reflections collected	2422
Space group	*Pbcn*	Independent reflections	2422 [*R* (int) = 0.0226]
a/Å	4.7071 (5)	Completeness to θ = 29.33°/%	97
b/Å	5.7097 (7)	Absorption correction	Semi-empirical from equivalents
c/Å	5.1111 (6)	Refinement method	Full-matrix least-squares on F^2
Volume/nm^3	137.37 (3)		
Z	4	Goodness-of-fit on F^2	0.94
D_c/(g·cm^{-3})	2.571	Final *R* indices [$I > 2\sigma(I)$]	R_1 = 0.031, wR_2 = 0.110
Absorption coefficient/mm^{-1}	8.139	Largest diff. peak and hole/(e·nm^{-3})	1.32 and −1.25
F (000)	228		

Table 5. Atom coordinates, displacement parameters, anisotropic displacement parameters, and bond distances for nioboixiolite-(☐).

Atom coordinates and displacement parameters (Å^2)						
Atom	Wyck.	Occupancy	x	y	z	U_{iso}
Nb1	4*c*	0.877(19)	1/2	0.83206(10)	1/4	0.0199(4)
O1	8*d*	1	0.2288(5)	0.6169(4)	0.4165(8)	0.0190(11)
Anisotropic displacement parameters (in Å^2)						
Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Nb1	0.0238(6)	0.0169(6)	0.0190(6)	0.000	0.00020(18)	0.000
O1	0.0225(16)	0.0145(14)	0.0200(17)	0.0021(13)	−0.0035(13)	0.0000(9)
Bond distances (Å)						
Nb1–O1	1.965(3) × 2					
–O1	2.037(4) × 2					
–O1	2.128(3) × 2					
Mean	2.043					

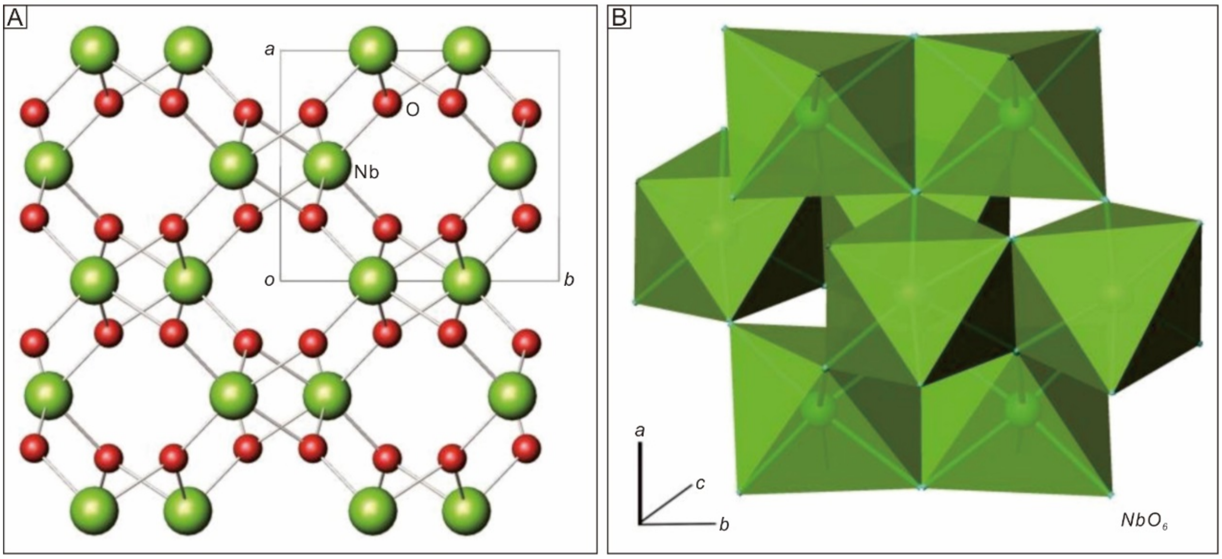

Figure 7. (**A**) Crystal structure of nioboixiolite-(☐) viewed from above [001], where the atoms of Nb and O are shown as green and red balls, respectively; (**B**) edge-sharing chains of Nb-O octahedra (NbO_6).

4. Discussion

There are numerous minerals that have the general formula of M_1O_2 (M = Ti^{4+}, Sn^{4+}, $^{VI}Ge^{4+}$, ^{VI}Si, $^{VI}Mn^{4+}$, $^{VI}Pb^{4+}$, $^{VI}Te^{4+}$, Nb^{5+}, Ta^{5+}, Sb^{5+}-, Mo^{6+}-, and W^{6+}) (Table 6) and are characterized by the same crystal structure as that of ixiolite (orthorhombic, *Pbcn*, $a = a_0$, $b = b_0$, $c = c_0$, and Z = 4) (Table 7). The Nb-dominant analogue of ixiolite (with Nb > Ta) has been known for a long time [2–5]. The scandian ixiolite from the Antsirable area, Madagascar, contains Nb_2O_5 at 63.28%, with subordinate Fe, Mn, and minor Sc [3]. The tantalum-free niobium analogue of ixiolite from the Laach Lake area (Eifel, Germany), has the empirical formula $(Nb_{1.55}Ti_{1.11}Fe^{3+}{}_{1.01}Mn^{2+}{}_{0.19}Cr^{3+}{}_{0.04}Mg_{0.04}Al_{0.03}Zr_{0.02}Mn^{3+}{}_{0.01})\ \Sigma_4O_8$ (Z = 1) [5]. Nioboixiolite-(Mn^{2+}) discovered in the Sosedka granitic pegmatite vein, Malkhan pegmatite field, Zabaikalsky Krai (Transbaikal Region), Siberia, Russia [2], is also isostructural with minerals of the ixiolite group, with the empirical formula $(Nb_{1.59}Mn^{2+}{}_{1.04}Ta_{0.59}Ti_{0.47}Sc_{0.13}Zr_{0.07}Y_{0.06}Sn_{0.03}U_{0.03}Fe^{3+}{}_{0.01})\ \Sigma_{4.02}O_8$ (Z = 1).

Nioboixiolite-(☐) has the same crystal structure as the above minerals and is also Nb-dominated. However, according to the nomenclature of columbite supergroup minerals [1], although there is only one cationic M1 site in the ixiolite-type structure, charge-balanced end-member formulae of ixiolite and its Nb-dominant analogue cannot be written with a single cationic component [1]. Thus, the dominant-charge-compensating cations (either a lower-valency cation or vacancy) should be taken into account, as discussed by Hatert and Burke [16]. The charge-compensating cations of the M1 site are Fe^{2+}, Mn^{2+}, and minor Sc^{3+} in the ixiolite-(Fe^{2+}), nioboixiolite-(Mn^{2+}), and tantalum-free ixiolite, respectively, and that of nioboixiolite-(☐) is a vacancy.

However, there are two core issues in relation to nioboixiolite-(☐) that should be discussed in detail: the first is whether it is a heterogeneous material. The second concerns the high uranium content.

Regarding the first issue, we believe that nioboixiolite-(☐) absolutely occurs naturally; it is not a mixture of uranium-bearing metamict and some crystalline minerals, but mineral particles may be impure and may contain some nano inclusions of other phases. First, on the micron scale, the chemical composition of nioboixiolite-(☐) is uniform, stable, and repeatable. The distribution of chemical component analysis spots (spot size of less than 5 μm) of the type specimen particle which was used for crystal structural analysis is shown in Figure S1; for the analysis results, see Table S1. Excluding numbers 15 and 28 (the data deviate significantly from the normal range), the analysis results of the remaining 38 spots are basically consistent. To verify the repeatability of the test analysis results, we found another particle (Figure S2) and adopted the same test methods and test conditions with the type specimen particle (for the analysis results, see Table S2; we obtained the same results as those in Table S1). The main components of nioboixiolite-(☐) are Nb, U, Ta, Ti, Si, Sr, and Fe (>1%). Second, nioboixiolite-(☐) has a distinctly different crystal structure to columbite-(Fe). As shown in Figure 6 and Table 7, we obtained the X-ray powder diffraction pattern and unit cell parameters of nioboixiolite-(☐) and columbite-(Fe). The figure and table show that nioboixiolite-(☐) and columbite-(Fe) are two different kinds of mineral. It is therefore impossible that nioboixiolite-(☐) is a mixture of metamict and columbite-(Fe) crystalline minerals.

Concerning the second issue, the core question is that of why nioboixiolite-(☐) has not completely metamictized given that it contains ~20% UO_3 and how to deal with the U^{6+} ion when calculating the empirical formula of nioboixiolite-(☐) given its different ionic radius to Nb^{5+}, Ta^{5+}, Ti^{4+}, and Fe^{3+}. Nioboixiolite-(☐) has a different X-ray powder diffraction pattern to columbite-(Fe) (Figure 6), so the obtained structural data are certainly not from uranium-bearing metamict columbite. However, this raises the question of why nioboixiolite-(☐) did not completely metamictize. It may be that the high amount of U^{6+} has partially metamictized the mineral and that Si, Ca, and Sr are simply diffused in glassy material. The evidence indicates that there is a U-O signal in the IR absorption spectrum and the Raman spectrum (Figures 3 and 4). Further evidence indicates that we cut a small piece of the particle, as shown in Figure S2, for single-crystal X-ray diffraction but we did not obtain the crystal data, which suggests that some nioboixiolite-(□) was metamictized. In this situation, these elements (U, Si, Ca, Sr) should not be used for formula normalization. The amounts of REE and Th, Pb, and Mg are very minor in the mineral (<0.05 apfu with an 8 O pfu) (Table 2) and can be ignored when calculating the formula. Thus, the nioboixiolite-(□) empirical formula only considers Nb, Ta, Ti, and Fe as four kinds of elements. The content of each element is 100% normalization when calculating the number of cations.

Nioboixiolite-(□) may be a new mineral formed via the fluid (enriched Si, U, Ca, Sr) replacement of early-stage columbite. It is chemically related to columbite-(Fe), $Fe^{2+}Nb_2O_6$, and the two are usually present in pairs; according to petrographic interpretation, the latter is replaced by the former (Figure 2C). Figure S2 shows an obviously metasomatic relict texture. The BSE image of minerals can be divided into two parts, the composition of the higher BSE signal part being similar to that of nioboixiolite-(□), and the lower BSE signal part composition having dramatically lower Nb and U and higher Ta and Si than nioboixiolite-(□) (Table S2, numbers 10–14). The change in these elements' contents may be caused by the migration of elements during fluid metasomatism. As shown in Figure 2C, nioboixiolite-(□) intergrowth was associated with columbite-(Fe), with the columbite-(Fe) being replaced by nioboixiolite-(□), the latter likely as a metasomatic relict of the former. Thus, it can be considered a cation-disordered analogue of columbite-(Fe) via the heterovalent substitution 12 Ta^{5+} + 5 [vac] = 10 Nb^{5+} + 5 Fe^{2+}.

An overwhelming majority of the discoveries of ixiolite and its Nb-dominant analogue, forming a continuous isomorphous series, are related to Li-F granites and, especially, rare-element granitic pegmatites [2]. However, nioboixiolite-(□) is related to carbonatite. It may have a certain genetic relationship with columbite widely developed in carbonate rocks. All samples of ixiolite group minerals from granite formations contain significant amounts of Ta, and those from carbonatite formations may be rich in Nb.

The crystal structure of a natural niobium analogue of ixiolite has only been published in recent years [2,5]. The crystal structure of an unusual Ta- and Sn-free and Ti- and Fe-rich sample from the Eifel paleovolcanic region, Germany, was provided by Zubkova et al., 2020. However, a detailed investigation of this sample was not carried out due to the scarcity of available material. A new ixiolite group mineral, nioboixiolite-(Mn^{2+}), ideally the niobium analogue of ixiolite-(Mn^{2+}), was discovered in the Sosedka granitic pegmatite vein, Malkhan pegmatite field, Zabaikalsky Krai (Transbaikal Region), Siberia, Russia [2]. Nioboixiolite-(□) has a different charge-compensating cation of M1 to nioboixiolite-(Mn^{2+}), with a vacancy instead of Mn^{2+}, just as their end-member formula shows.

Synthetic Nb-dominant oxides that are isostructural with ixiolite have been described in a number of studies. In particular, the crystal structures of the compounds $Fe^{3+}NbO4$–II [17], $Nb_xFe^{3+}{}_xZn_{1-x}$, $O_{4x}F_{2-2x}$ (with x from 0.75 to 1.00: [18]), and Nb_2TiZnO_8 [19] have been investigated [2]. All of them belong to the α-PbO2 structure type. However, single-phase synthetic NbO_2 has a distorted rutile structure (space group $I41/a$) to rutile structure (space group $P42/mnm$) from a low temperature phase to a high temperature phase at approximately 800 °C [20].

Comparative data for nioboixiolite-(□) and closely related minerals are given in Table 7. The *M*-O distances in the polyhedra of nioboixiolite-(□) are somewhat shorter than those of nioboixiolite-(Mn^{2+}) and ixiolite-(Fe^{2+}) (Table 8), but the overall difference is not much. All of them have the same unit cell parameters.

Table 6. Chemical analyses of nioboixiolite-(□), nioboixiolite-(Mn^{2+}), ixiolite, columbite-(Fe), scandian ixiolite, rossovskyite, and wodginite.

Contents	Nioboixiolite-(□)	Nioboixiolite-(Mn^{2+})	Ixiolite-(Fe^{2+})	Columbite-(Fe)	Scandian Ixiolite	Rossovskyite	Wodginite
Nb_2O_5	47.04	42.80	10.50	73.18	63.28	26.59	1.35
Ta_2O_5	13.95	26.77	61.47	6.12	5.82	37.51	70.05
UO_3	21.56	1.44	-	0.02			-
TiO_2	3.68	7.66	0.38	0.26	6.54	7.69	2.39
Fe_2O_3	3.57	0.2	8.08	15.03 b	8.16 f	20.58 a	1.87
CaO	2.76	-	0.11	0.89			-
SiO_2	1.69	-	0.12	0.15			0.6
REE_2O_3	1.58	1.34 d	-	0.07	2.12		-
MnO	0.12	14.94	5.40	1.63	9.65	1.68	9.04
PbO	0.91		-	0.26			
ThO_2	0.11	0.26	-	0.06			-
MgO	0.15		-	1.90			-
$ZrOb_2$	-	1.74	0.60	-			-
F	0.01		-	0.21			
SnO_2	-	1.01	12.27	-	0.2		13.2
Al_2O_3	0.01		0.16	-			-
Sc_2O_3		1.80			2.1		
WO_3			0.30	-		5.61	-
BaO	0.62						
SrO	1.49						
H_2O^+			0.16				-
$H_2O(-)$			0.08				-
Total	99.25	99.96	99.63	99.78	99.37	99.66	98.50
Reference	This study	[2]	[21]	This study	[3]	[22]	[23]

a The sum of FeO (5.92) and Fe_2O_3 (14.66); b Fe is divalent; d is Y_2O_3; f is the sum of FeO (6.84) and Fe_2O_3 (1.32).

Table 7. Comparison of unit cell parameters for nioboixiolite-(□), nioboixiolite-(Mn^{2+}), ixiolite-(Fe^{2+}), and columbite-(Fe).

Mineral	Nioboixiolite-(□) Bayan Obo, China	Nioboixiolite-(Mn^{2+}), Sosedka, Russia	Ixiolite-(Fe^{2+}) Skogsböle, Finland	Columbite-(Fe) Bayan Obo, China
a (Å)	5.7097	4.7559	5.731	5.709
b (Å)	4.7071	5.7318	4.742	14.150
c (Å)	5.1111	5.1344	5.152	5.094
β (°)	90	90	90	90
V (Å3)	137.37	139.97	140	414
Symmetry	Orthorhombic	Orthorhombic	Orthorhombic	Orthorhombic
Space Group	*Pbcn*	*Pbcn*	*Pbcn*	*Pbcn*
Simplified Formula	$(Nb_{0.8}\square_{0.2})^{4+}O_2$	$(Nb_{2/3}Mn^{2+}{}_{1/3})O_2$	$(Ta_{2/3}Fe^{2+}{}_{1/3})O_2$	$Fe^{2+}Nb_2O_6$
Reference	This study	[2]	[23]	This study

Table 8. Cation-oxygen distances (Å) in the structure of nioboixiolite-(□), nioboixiolite-(Mn^{2+}), and ixiolite.

Bond Distances (Å)	Nioboixiolite-(□)	Nioboixiolite-(Mn^{2+})	Ixiolite-(Fe^{2+})
M–O1	1.965(3) × 2	1.984(7) × 2	2.04(4) × 2
–O1	2.037(4) × 2	2.052(8) × 2	1.99(4) × 2
–O1	2.128(3) × 2	2.137(7) × 2	2.16(4) × 2
Mean	2.043	2.058	2.06
Reference	This study	[2]	[6]

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/min15010088/s1, Figure S1: Distribution of chemical component analysis points of the nioboixiolite-(□); Figure S2: Distribution of chemical component analysis spots (blue pentagon, number1-19) of the nioboixiolite-(□) from another particle; Table S1: The chemical component analysis result of nioboixiolite-(□) from type specimen; Table S2: The chemical component analysis result of nioboixiolite-(□) from another particle; Table S3: The reflectance of nioboixiolite-(□).

Author Contributions: Y.L., C.K. and D.W. conceived of the presented study. Y.L. discovered the nioboixiolite-(□) specimen for the first time. Y.L., C.K., L.Z., Y.G. and B.G. carried out the field work. G.L., R.L. and H.Y. carried out the experiments. Z.C. verified the analytical methods. C.K. and Z.P. prepared all the figures in the manuscript. D.W. and Y.Z. encouraged Y.L. and C.K. to investigate a specific aspect of the research and supervised the findings of this work. All authors discussed the results and contributed to the final manuscript. All authors have read and agreed to the published version of the manuscript.

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Institutional Review Board Statement: The new mineral nioboixiolite-(□) and its name were approved by the IMA-CNMNC (IMA No. 2021-02a).

Informed Consent Statement: Informed consent was obtained from all subjects involved in this study.

Data Availability Statement: All research data have been included in the manuscript; no new data were created.

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References

1. Chukanov, N.V.; Pasero, M.; Aksenov, S.M.; Britvin, S.N.; Zubkova, N.V.; Li, Y.K.; Witzke, T. Columbite supergroup of minerals: Nomenclature and classification. *Mineral. Mag.* **2023a**, *87*, 18–33. [CrossRef]
2. Chukanov, N.V.; Pekov, I.V.; Zubkova, N.V.; Yapaskurt, V.O.; Shelukhina, Y.; Britvin, S.N.; Pushcharovsky, D.Y. Nioboixiolite-(Mn^{2+}), ($Nb_{2/3}Mn^{2+}{}_{1/3}$) O_2, a new ixiolite-group mineral from the Malkhan pegmatite field, Transbaikal region, Russia. *Proc. Russ. Mineral. Soc.* **2023b**, *CLII*, 8–17.
3. von Knorring, O.V.; Sahama, T.G. Scandian ixiolite from Mozambique and Madagascar. *Bull. Geol. Soc. Finl.* **1969**, *41*, 75–77. [CrossRef]
4. Wise, M.A.; Černý, P.; Falster, A.U. Scandium substitution in columbite-group minerals and ixiolite. *Can. Minerogist* **1998**, *36*, 673–680.
5. Zubkova, N.V.; Chukanov, N.V.; Pekov, I.V.; Ternes, B.; Schüller, W.; Pushcharovsky, D.Y. Tantalum-free Nb-dominant analogue of ixiolite from the Eifel paleovolcanic region, Germany, and its crystal structure: On the problem of "ashanite". *Zap. Ross. Mineral. Obs.* **2020**, *149*, 125–134. (In Russian)
6. Grice, J.D.; Ferguson, R.B.; Hawthorne, F.C. The crystal structures of tantalite, ixiolite and wodginite from Bernic Lake, Manitoba. I. Tantaliteand ixiolite. *Can. Mineral.* **1976**, *14*, 540–549.
7. Nordenskiöld, A.E. Beitrag zu Finnlands Mineralogie. *Ann. Phys. Chem.* **1857**, *11*, 625–642. [CrossRef]
8. Taggart, J.E., Jr.; Foord, E.E.; Rosenzweig, A.; Hanson, T. Scrutinyite, natural occurrences of PbO_2 from Bingham, New Mexico, U.S.A., and Mapimi, Mexico. *Can. Mineral.* **1988**, *26*, 905–910.
9. Willgallis, A.; Siegmann, E.; Hettiaratchi, T. Srilankite, a new Zr-Ti-oxide mineral. *Neues Jahrb. Mineral. Monatshefte* **1983**, *1983*, 151–157.

10. Dera, P.; Prewitt, C.T.; Boctor, N.Z.; Hemley, R.J. Characterization of a high-pressure phase of silica from the Martian meteorite Shergotty. *Am. Mineral.* **2002**, *87*, 1018–1023. [CrossRef]
11. Hu, L.; Li, Y.; Sun, S.; Li, R.; Ke, C.; Wang, A. Identification of new igneous carbonatites in the Bayan Obo area, Inner Mongolia. *Geol. China* **2023**, *50*, 1788–1803, (In Chinese with English Abstract).
12. Strehle, M. *X-Ray Photoelectron Spectroscopy (XPS) Study of Single Crystal UO_2 and U_3O_8 on R-Plane Sapphire and Yttrium Stabilized Zirconium (YSZ) Substrates (Mater Dissertation)*; University of Illinois Urbana-Champaign: Champaign, IL, USA, 2011; pp. 1–64.
13. Palacio, C.; Mathieu, H.J.; Stambouli, V.; Landolt, D. XPS study of in-situ oxidation of an Fe-Cr alloy by low pressure oxygen in the presence of water vapor. *Surf. Ence Lett.* **1993**, *295*, 251–262. [CrossRef]
14. Sheldrick, G.M. SHELXT-Integrated space-group and crystal structure determination. *Acta Crystallogr.* **2015**, *A71*, 3–8. [CrossRef] [PubMed]
15. Sheldrick, G.M. Crystal structure refinement with SHELX. *Acta Crystallogr.* **2015**, *C71*, 3–8.
16. Hatert, F.; Burke, E.A.J. The IMA-CNMNC dominant-constituent rule revisited and extended. *Can. Mineral.* **2008**, *46*, 717–728. [CrossRef]
17. Harrison, W.T.A.; Cheetham, A.K. Structural and magnetic properties of $FeNbO_4$-II. *Mater. Res. Bull.* **1989**, *24*, 523–527. [CrossRef]
18. Pourroy, G.; Lutanie, E.; Poix, P. Transition orthorhombic ↔ rutile in $xMFeO_4$-$(1-x)$ ZnF_2 phases (M = Ta, Nb and $x > 0.7$). *J. Solid State Chem.* **1990**, *86*, 41–49. [CrossRef]
19. Baumgarte, A.; Blachnik, R. Phase relations in the system titaniumdioxide-diniobium-zinc-hexoxide. *Mater. Res. Bull.* **1992**, *27*, 1287–1294. [CrossRef]
20. Hadamek, T.; Posadas, A.B.; Dhamdhere, A.; Smith, D.J.; Demkov, A.A. Spectral identification scheme for epitaxially grown single-phase niobium dioxide. *J. Appl. Phys.* **2016**, *119*, 095308. [CrossRef]
21. Nickel, E.H.; Rowland, J.F.; McAdam, R.C. Ixiolite—A columbite substructure. *Am. Mineral.* **1963**, *48*, 961–979.
22. Konovalenko, S.I.; Ananyev, S.A.; Chukanov, N.V.; Rastsvetaeva, R.K.; Aksenov, S.M.; Baeva, A.A.; Gainov, R.R.; Vagizov, F.G.; Lopatin, O.N.; Nebera, T.S. A new mineral species rossovskyite, $(Fe^{3+},Ta)(Nb,Ti)O_4$: Crystal chemistry and physical properties. *Phys. Chem. Miner.* **2015**, *42*, 825–833. [CrossRef]
23. Nickel, E.H.; Rowland, J.F.; McAdam, R.C. Wodginite—A new tin-manganese tantalate from Wodgina, Australia and Bernic lake, Manitoba. *Can. Mineral.* **1963**, *7*, 390–402.