# Isolueshite: a new mineral of the perovskite group from the Khibina alkaline complex

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**Abstract:** Isolueshite, ideally (Na, La, Ca) (Nb, Ti)O<sub>3</sub>, was found in a hydrothermally altered pegmatite vein in ijolite-urtite of the Khibina alkaline complex, Kola Peninsula, Russia. The host rock consists of microcline, sodalite, aegirine, arfvedsonite and lamprophyllite. Isolueshite occurs as scarce euhedral crystals and their occasional intergrowths enclosed in microcline and sodalite. The crystals reach 0.3 mm in diameter and are a combination of cube and rhombic dodecahedron. The mineral is opaque, optically isotropic, brownish-black in colour; n 2.20(1); some reflectance values are [R, % ( $\lambda$ , nm)]: 16.55 (440), 15,50 (500), 14.80 (560), 14.45 (620), 14.35 (680). Density is 4.72(1)<sub>meas</sub>, 4.69<sub>calc</sub>; VHN<sub>70</sub> ranges from 479 to 616. Back-scattered electron imagery revealed a pronounced zonation of isolueshite. The structural formulae calculated from electron microprobe analyses of different zones fall into the following range: (Na<sub>0.66-0.73</sub> La<sub>0.05-0.08</sub> Ce<sub>0.03-0.08</sub> Nd<sub>0-0.01</sub> Ca<sub>0.05-0.08</sub> Sr<sub>0.02-0.03</sub> Th<sub>0.01-0.03</sub>) (Nb<sub>0.52-0.66</sub> Ti<sub>0.35-0.49</sub>) O<sub>3.00</sub>. The mineral is cubic (space group *Pm3m*), *a* = 3.911(3) Å, *Z* = 1. The five strongest X-ray diffraction lines are [d<sub>meas</sub>. in Å (I) (hkl)]: 3.915 (35) (100), 2.765 (100) (110), 1.953 (53) (200), 1.594 (30) (211), 1.380 (22) (220). The compositional features of isolueshite suggest that the mineral is a stabilised polymorph of NaNbO<sub>3</sub>. The name is for isometric habit and optical isotropism of the mineral, compared with the orthorhombic polymorph lueshite. Cotype samples are deposited in the Mining Museum of the Mining Institute, St. Petersburg, and in the Mineralogical Museum of St. Petersburg State University, Russia.

Key-words: new mineral, isolueshite (Na, La, Ca) (Nb, Ti)O<sub>3</sub>, lueshite, natroniobite, perovskite group, Khibina complex, Kola Peninsula.

# Introduction

The Khibina alkaline complex, Kola Peninsula, Russia, covering an area of 1327 sq. km is the largest body of nepheline syenites and allied rocks in the world. The complex emplaced into Archean granite gneisses and Proterozoic volcanic-sedimentary lithologies consists of (from the western contact inwards): umptektite and nepheline syenite, massive and trachytic khi-

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binites, foidolite series associated with poikilitic nepheline syenite (rischorrite), massive and trachytic foyaites, carbonatite (Sørensen, 1970; Kostyleva-Labuntsova *et al.*, 1978; Kogarko *et al.*, 1995). The rocks of the Khibina complex have been dated at  $362.4 \pm 4.5 - 377.3 \pm 3.9$  Ma (Kramm *et al.*, 1993).

Until recently, only two perovskite-group minerals were known to occur at Khibina: perovskite in ultrabasic xenoliths and foidolites (Shilin & Yanchenko, 1962; Shpachenko et al., 1990), and loparite-(Ce) in nepheline syenites, associated pegmatites and metasomatites (Kuznetsov, 1925; Tikhonenkova et al., 1982; Bel'kov et al., 1988; Chakhmouradian et al., 1995). In 1957, Tikhonenkov & Kazakova described "nioboloparite" as a new species (Tikhonenkov & Kazakova, 1957). Subsequently, "nioboloparites" have been found at several localities in the Khibina and Lovozero complexes, Kola Peninsula (Semenov, 1972; Shliukova & Unanova, 1972; Kostyleva-Labuntsova, 1978), and in the Schryburt Lake complex, Ontario, Canada (Platt, 1994). Neotype samples of Tikhonenkov & Kazakova's "nioboloparite" have been re-investigated by Mitchell et al. (1996). These authors have proved this mineral to be ordinary loparite-(Ce) with an average Nb<sub>2</sub>O<sub>5</sub> content of 11 wt.% and suggested that the name "nioboloparite" should be abandoned as a valid mineral name.

First samples of isolueshite were found by one of the authors (VYa) at the Kukisvumchorr underground apatite mine, southern Khibina, in 1991. The samples were preliminary studied by Mitchell *et al.* (1996) who classified the mineral as lanthanian lueshite on the basis of its composition. Subsequently undertaken single-crystal Xray analysis and optical investigation indicated that this mineral was a new mineral species which, unlike compositionally similar lueshite, had a cubic symmetry.

Isolueshite was named according to its isometric habit, optical isotropism and compositional similarity to the orthorhombic NaNbO<sub>3</sub> polymorph lueshite (Safiannikoff, 1959). Both the mineral and its name were approved by the Commission on New Minerals and Mineral Names, IMA (vote 95-024). Cotype samples are deposited in the Mining Museum of the Mining Institute, St. Petersburg, under catalogue number 3007, and in the Mineralogical Museum of St. Petersburg State University, Russia, under catalogue number 1/18271.



Fig. 1. Geological setting and zonation of isolueshitebearing hydrothermally altered pegmatite vein. Kukisvumchorr apatite deposit, south Khibina. 1 ijoliteurtite, 2 contact zone, 3 intermediate zone, 4 cavernous zone.

### Occurrence

Isolueshite occurs in a hydrothermally altered pegmatite vein (Fig. 1) cutting ijolite-urtite (1) at the Kukisvumchorr apatite deposit (southern part of the complex). There are three zones distinguished within the vein: a microcline-sodaliteaegirine zone with arfvedsonite and lamprophyllite as minor phases at the contact (2); an intermediate zone composed of natrolite, pectolite, lamprophyllite, astrophyllite and fersmanite (3); a series of cavities up to 0.5 m across with crystals and spherulites of natrolite and calcite (4). Isolueshite is found only in the contact zone as euhedral crystals and their intergrowths enclosed in microcline and sodalite. The crystals of isolueshite include scarce microlaths of microcline and isometric grains of Th-rich titaniumniobium oxide, probably pyrochlore.

# Physical and optical properties

Isolueshite crystals are a combination of cube and rhombic dodecahedron, and reach 0.3 mm in size. {110} faces are fine-striated parallel to the edges common with cube faces (Fig. 2a). The mineral is brownish-black with pale-yellow streak and adamantine lustre, brittle with uneven fracture. There is no evidence of the pseudocubic cleavage typical of lueshite and perovskite.



Fig. 2. Morphology and zonation of isolueshite. a - SEM photograph of a crystal. Scale bar is 0.2 mm; b - zonation pattern. Schematic drawing of a back-scattered electron image.

The microhardness (70-g indentor) is slightly higher on {110}, compared to {100}: 544-616 and 479-544, respectively. An average microhardness of 580 corresponds to 5.5 on the Mohs' scale. The measured density is 4.72(1) g/cm<sup>3</sup> (average of three measurements by microburette method); the calculated density is 4.69 g/cm<sup>3</sup> based on the empirical formula and the measured unit-cell parameters, Z = 1.

Isolueshite is optically isotropic in fine pieces. Under reflected light, the mineral is bluish with internal reddish-brown reflections. Reflectance values obtained as average of four measurements are given in Table 1. Refractive index (S-Se media) is 2.20(1) which is close to 2.22 calculated from reflectance values at 660-700 nm (redorange range of the visible spectrum).

Table 1. Reflectance values of isolueshite.

R, %	λ, nm
440	16.55
460	16.05
480	15.75
500	15.50
520	15.25
540	15.00
560	14.80
580	14.70
600	14.55
620	14.45
640	14.40
660	14.35
680	14.35
700	14.35

An infra-red absorption spectrum of the mineral was obtained on a Zeiss UR-20 spectrometer (KBr-pellet). Two major absorption bands at 415 cm<sup>-1</sup> and 600 cm<sup>-1</sup>, as well as a general spectrum pattern indicate correspondence of isolueshite to the perovskite group.

## **Chemical composition**

A preliminary study of the mineral in backscattered electrons has revealed its complex zonation (Mitchell *et al.*, 1996). There are four distinct zones within the crystal that significantly differ in composition; the zones are generally parallel to the {100} faces (Fig. 2b).

Compositions of the different zones were determined by wavelength dispersive method (WDS) using a Cameca SX-50 electron microprobe following the analytical scheme utilised by Mitchell & Vladykin (1993). Except LREEs, all elements were determined at an accelerating voltage of 15 kV and beam current 20 nA, the light rare earths at 20 kV and 40 nA, respectively. Standards used for the microprobe work are reported in Table 2.

Table 2 gives the representative chemical compositions and structural formulae of different zones within the crystal. The assignment of Th to the twelve-coordinated A-sites achieves better stoichiometry of the formulae and is corroborated by its ionic radius in a twelve-coordinated polyhedron (1.21 Å: Shannon, 1976), although the site preference for Th in Na and Nb-enriched

	1	2	3	4	
Na <sub>2</sub> O	13.65	12.82	12.05	12.28	
K₂O	0.07	0.06	0.09	0.04	
CaO	2.82	2.25	2.16	1.48	
SrO	2.03	2.02	1.66	1.42	
La₂O₃	5.17	7.80	7.08	7.83	
Ce <sub>2</sub> O <sub>3</sub>	3.12	5.07	5.08	7.44	
Pr <sub>2</sub> O <sub>3</sub>	0.15	0.20	0.21	0.45	
Nd <sub>2</sub> O <sub>3</sub>	0.18	0.33	0.47	0.82	
Sm <sub>2</sub> O <sub>3</sub>	n.d	n.d	n.d	0.03	
ThO₂	1.15	2.41	4.88	2.98	
FeO <sub>T</sub> *	0.02	0.03	n.d	0.02	
TiO₂	17.05	21.08	22.24	23.00	
Nb <sub>2</sub> O <sub>5</sub>	53.41	44.23	41.81	40.68	
Ta <sub>2</sub> O <sub>5</sub>	0.58	0.79	0.64	0.39	
Total	99.40	99.09	98.37	98.86	

Table 2. Compositions (wt.%) and structural formulae of isolueshite.

1  $(Na_{0.73} La_{0.05} Ce_{0.03} Ca_{0.08} Sr_{0.03} Th_{0.01})_{0.93} (Nb_{0.66} Ti_{0.35})_{1.01} O_{3.00}$ 

 $2 \hspace{0.1in} (Na_{0.70} \hspace{0.1in} La_{0.08} \hspace{0.1in} Ce_{0.05} \hspace{0.1in} Ca_{0.07} \hspace{0.1in} Sr_{0.03} \hspace{0.1in} Th_{0.02})_{0.95} \hspace{0.1in} (Nb_{0.56} \hspace{0.1in} Ti_{0.45} \hspace{0.1in} Ta_{0.01})_{1.02} \hspace{0.1in} O_{3.00}$ 

3  $(Na_{0.66} La_{0.07} Ce_{0.05} Ca_{0.07} Sr_{0.03} Th_{0.03})_{0.91} (Nb_{0.54} Ti_{0.48})_{1.02} O_{3.00}$ 

 $(Na_{0.68} La_{0.08} Ce_{0.08} Nd_{0.01} Ca_{0.05} Sr_{0.02} Th_{0.02})_{0.94} (Nb_{0.52} Ti_{0.49})_{1.01} O_{3.00}$ 

 $5 \hspace{0.2cm} (Na_{0.68} \hspace{0.2cm} La_{0.08} \hspace{0.2cm} Ce_{0.07} \hspace{0.2cm} Nd_{0.01} \hspace{0.2cm} Ca_{0.06} \hspace{0.2cm} Sr_{0.02} \hspace{0.2cm} Th_{0.02})_{0.94} \hspace{0.2cm} (Nb_{0.53} \hspace{0.2cm} Ti_{0.48})_{1.01} \hspace{0.2cm} O_{3.00}$ 

1 inner core, 2 outer core, 3 inner rim, 4 outer rim, 5 empirical formula. \* Total Fe as FeO. n.d ≈ not detected. All structural formulae calculated on the basis of 3 atoms of oxygen. Standards: albite (Na), almandine (Fe), diopside (Ca), microlite (Ta), monazite (Ce), olivine (Mg), orthoclase (K), spessartine (Mn), thorite (Th), witherite (Ba), metallic Pb, SrTiO<sub>2</sub> (Sr, Ti), LaVO<sub>4</sub> (La), ZrO<sub>2</sub>, Nb<sub>2</sub>O<sub>5</sub> and REE-bearing glasses (Pr, Nd, Sm) (Drake & Weill, 1972). Ba, Pb, Mg and Zr were sought, but not detected.

perovskite-type compounds is unknown. From Table 2, it is evident that isolueshite has the following compositional features:

i) Nb dominates over Ti in the six-coordinated B-sites.

ii) Na dominates over LREEs, Ca and other A-cations. It is noteworthy that La, not Ce, is a major element among REEs in isolueshite. The data available from the literature show that all previously analysed perovskite-group minerals are Ce-dominant species.

For instance, Ce/La ratio in loparites-(Ce) ranges between 1.2 and 2.3 (Chakhmouradian *et al.*, 1995; Haggerty & Mariano, 1983; Khomy-akov, 1972; Kozyreva *et al.*, 1991; Subbotina *et al.*, 1991). According to 18 microprobe determinations, the Ce/La ratio in isolueshite gradually increases from 0.5-0.6 at the core to 1.0 at the outer rim.

iii) Cation deficiency at the A-sites, which implies that some of the twelve-coordinated sites in the "rigid" framework of (Nb,Ti)O<sub>6</sub> are vacant. This phenomenon is well-known for synthetic tungsten bronzes  $M_xWO_3$  (0 < x < 1, M = K, Na, Ba, *etc.*) (Mitchell, 1996).

iv) The mineral compositionally evolves through Ti, Ce, Pr and Nd-enrichment, coupled with

depletion in Ca, Sr and Nb from the core toward the rim.

The ternary system lueshite NaNbO<sub>3</sub> - perovskite CaTiO<sub>3</sub> - NaLaTi<sub>2</sub>O<sub>6</sub> was chosen for graphic representation of the compositional evolution of isolueshite. NaLaTi<sub>2</sub>O<sub>6</sub> as a lanthanium analogue of loparite-(Ce) has not been found in nature, but has been synthesised and shown to possess the perovskite structure (Mitchell, 1996). Fig. 3 depicts the core-to-rim zonation trend observed in isolueshite. It is essentially from La-Ca-rich lueshite to La-rich lueshite nearly parallel to the NaNbO<sub>3</sub>-NaLaTi<sub>2</sub>O<sub>6</sub> join. Although all composition points of isolueshite fall within the lueshite field of the ternary plot, X-ray crystallography findings (see below) allow the distinction of this mineral as a new species.

The empirical formula of isolueshite (Table 2) was calculated on the basis of relative volume proportions occupied by compositionally different zones. The obtained empirical formula is very close to structural formula of the fourth zone occupying more than 70 % of crystal's volume (see Fig. 2b). The Gladstone-Dale relationship computed from the empirical formula (Mandarino, 1976 and 1981) is 0.010 (excellent correspondence).

Isolueshite, new perovskite-group mineral



Fig. 3. Compositions (mol.%) of isolueshite (1), lueshite (2) and loparites-(Ce) (3) in the ternary systems NaNbO<sub>3</sub>-CaTiO<sub>3</sub>-NaLaTi<sub>2</sub>O<sub>6</sub> and NaNbO<sub>3</sub>-CaTiO<sub>3</sub>-NaCeTi<sub>2</sub>O<sub>6</sub>. Data on lueshite from Mitchell (1996); data on loparites-(Ce) from Mitchell & Chakhmouradian (1996).

# X-ray crystallography

The X-ray diffraction (XRD) pattern of isolueshite was obtained on a DRON-2.0 diffractometer at a goniometer rotation rate of 0.25° per minute ( $CuK\alpha$  radiation, Ge internal standard). The XRD pattern of isolueshite is very similar to that of perovskite-type compounds with ideal cubic structure, for instance SrTiO<sub>3</sub> (ASTM file card 5-0636). Unlike the XRD pattern of orthorhombic lueshite (Table 3), that of isolueshite lacks weak reflections (e.g.  $d \approx 3.80; 3.12; 2.47$ ) and splittings of some strong lines (e.g.  $d \approx 3.88$ -3.91; 2.75-2.78). The unit-cell dimensions of isolueshite were refined from the XRD pattern by the least-squares method using the domestic PARAM program for PC (Table 3). Single-crystal X-ray studies by oscillating-crystal (camera RKV-86) and de Jong-Bouman (camera KFOR) methods confirmed the cubic symmetry of isolueshite (diffraction symbol m3mP). The space group of the mineral cannot be defined unequivocally because of the absences. By analogy with other cubic perovskite-type compounds, we suggest the space group *Pm3m* corresponding to aristotype structure (Megaw, 1973). Further studies of the isolueshite structure are being undertaken by H. R. Wenk (University of California at Berkeley).

#### Discussion

The above compositional and structural data indicate that isolueshite is a cubic polymorph of sodium niobate. It is well-known that cubic NaNbO<sub>3</sub> stable above 640°C undergoes several phase transitions with decreasing temperature (Ahtee *et al.*, 1972; Denoyer *et al.*, 1971; Glazer & Megaw, 1972; Ismailzade, 1963; Solov'ev *et al.*, 1961). The P-phase stable at room temperature is orthorhombic with space group *Pbcm* (Sakowski-Cowley *et al.*, 1969) or *Pbma* (Glazer, 1972). At the same time, the stable roomtemperature structural form of NaNbO<sub>3</sub> with 2.5 mol.% KNbO<sub>3</sub> is not the P-phase, but the Q-

Isolueshite						Lues	hite*			Natro	niobite <sup>#</sup>
hkl	I.	<b>d</b> <sub>meas</sub>	d <sub>calc</sub>	hkl	ŧ	d	hki	1	d	1	d
100	35	3.915	3.9110	101	90	3.912	143	20	1.5894	2	4.8
110	100	2.765	2.7655	040	45	3.882	191	1	1.5780	4	3.79
				111	1	3.797	203, 312	1	1.5314	2	3.36
200	53	1.953	1.9555	131	<1	3.122	182, 213	1	1.5252	3	3.29
				200	25	2.785	0.10.1	<1	1.4947	9	3.06
210	8	1.747	1.7491	141,002	100	2.754	400	3	1.3923	10	2.97
211	30	1.594	1.5967	102	1	2.468	371, 282	13	1.3779	2	2.79
220	22	1.380	1.3827	211, 230	1	2.453	253	8	1.3745	3	2.69
				112	1	2.435	411, 430	<1	1.3445	1	2.60
221	1	1.295	1.3037	221	1	2.366	104	<1	1.3362	1	2.47
300			1.3037	122	1	2.351	124, 2.10.1	<1	1.3164	3	2.39
310	7	1.234	1.2368	061	1	2.342	440	1	1.3105	1	2.30
				240	1	2.263	381	4	1.3032	2	2.25
				042	2	2.245	044, 183	5	1.2965	1	2.04
222	2	1.128	1.1290	241	<1	2.093	0.12.0, 134	3	1.2935	1	1.99
				202	25	1.9574	333	<1	1.2649	3	1.93
321	5	1.042	1.0453	080, 251	16	1.9400	402	2	1.2424	5	1.89
				023, 162	1	1.7857	412	3	1.2385	1	1.87
				301	7	1.7591	343	3	1.2369	2	1.76
				311, 242	12	1.7478	204	3	1.2336	6	1.72
				103	14	1.7432	1.12.1	5	1.2283	8	1.60
				181	16	1.7385	442	<1	1.1831	4	1.59
				331	1	1.6652	244	1	1.1757	4	1.544
				043	1	1.6593	0.12.2	1	1.1706	4	1.523
				341	11	1.6018	480	1	1.1311	2	1.481
_			(0)								
a <sub>0</sub> , /	. Δ	3.911	(3)			5 569	87(5)				
h	h				15.50	23(2)					
C	Ā					5 504	7(12)				
V, A	3	59,8	(1)			0.004	( ( <b>Z</b> )				

Table 3. Comparison between X-ray powder diffraction data of isolueshite, lueshite and natroniobite.

\* ASTM 33-1270. \* Kukharenko et al. (1965).

phase (Wells & Megaw, 1961). Transitions in which structural modifications are induced by changes in composition rather than by thermody-

namic factors are termed "stabilised polymorphism" and are well-known for naturally occuring TiO<sub>2</sub> and ZrO<sub>2</sub> (Smirnova & Belov, 1969).

Table 4. Morphology, physical and optical properties of isolueshite, lueshite and natroniobite.

	Isolueshite	Lueshite*	Natroniobite <sup>#</sup>	
Morphology	Cube + mombic dodecahedron	Pseudocube	Pseudomorphs after perovskite and pyrochlore	
Colour	brownish-black	black	yellow to brownish-black	
Anisotropism	isotropic	anisotropic	anisotropic	
Refractive	2.20(1)	2.30	2.10-2.24	
Mohs' hardness	5.5	5.5	5.5-6	
Microhardness	479-616	-	-	
Density	4.72(1)	4.44	4.40	
Cleavage	none	pseudocubic	none	

\* Safiannikoff (1959). \* Kukharenko et al. (1965).

Significant amounts of LREE and Ti in the isolueshite suggest that this mineral is a LREE-Ti-stabilised polymorph of NaNbO<sub>3</sub>. The other natural NaNbO<sub>3</sub> polymorph is lueshite first described from the Lueshe carbonatite complex, Zaire (Safiannikoff, 1959). This author has determined for lueshite the space group *P*222<sub>1</sub> which differs from that of synthetic NaNbO<sub>3</sub> at room temperature (see above). The recently reinvestigated composition of lueshite is close to theoretical: (Na<sub>0.855</sub> Ca<sub>0.031</sub> Ce<sub>0.011</sub> La<sub>0.005</sub> Nd<sub>0.003</sub>) Pr<sub>0.002</sub> Th<sub>0.003</sub>)<sub>0.910</sub> (Nb<sub>0.959</sub> Ti<sub>0.049</sub> Ta<sub>0.003</sub>)<sub>1.011</sub> O<sub>3</sub> (Mitchell, 1996, Table 5).

In most recently published glossaries of mineral species, natroniobite is considered as a monoclinic polymorph of NaNbO3 (e.g. Fleisher & Mandarino, 1995). This mineral has been discovered in a number of carbonatite complexes at the Kola Peninsula and then described in detail by Kukharenko et al. (1965). The empirical formula of natroniobite NaNb2O5OH and the close resemblance between X-ray diffraction patterns of natroniobite and fersmite CaNb2O6 suggest that both minerals are isostructural (Kukharenko et al., 1965). Therefore, natroniobite should be regarded as a sodium-analogue of fersmite rather than a monoclinic polymorph of NaNbO<sub>3</sub>. The X-ray diffraction data of isolueshite, synthetic lueshite and natroniobite are compared in Table 3. Morphology, physical and optical properties of isolueshite, naturally occuring lueshite and natroniobite are given in Table 4.

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# Isolueshite: a new mineral of the perovskite group from the Khibina alkaline complex

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**Abstract:** Isolueshite, ideally (Na, La, Ca) (Nb, Ti)O<sub>3</sub>, was found in a hydrothermally altered pegmatite vein in ijolite-urtite of the Khibina alkaline complex, Kola Peninsula, Russia. The host rock consists of microcline, sodalite, aegirine, arfvedsonite and lamprophyllite. Isolueshite occurs as scarce euhedral crystals and their occasional intergrowths enclosed in microcline and sodalite. The crystals reach 0.3 mm in diameter and are a combination of cube and rhombic dodecahedron. The mineral is opaque, optically isotropic, brownish-black in colour; n 2.20(1); some reflectance values are [R, % ( $\lambda$ , nm)]: 16.55 (440), 15,50 (500), 14.80 (560), 14.45 (620), 14.35 (680). Density is 4.72(1)<sub>meas</sub>, 4.69<sub>calc</sub>; VHN<sub>70</sub> ranges from 479 to 616. Back-scattered electron imagery revealed a pronounced zonation of isolueshite. The structural formulae calculated from electron microprobe analyses of different zones fall into the following range: (Na<sub>0.66-0.73</sub> La<sub>0.05-0.08</sub> Ce<sub>0.03-0.08</sub> Nd<sub>0-0.01</sub> Ca<sub>0.05-0.08</sub> Sr<sub>0.02-0.03</sub> Th<sub>0.01-0.03</sub>) (Nb<sub>0.52-0.66</sub> Ti<sub>0.35-0.49</sub>) O<sub>3.00</sub>. The mineral is cubic (space group *Pm3m*), *a* = 3.911(3) Å, *Z* = 1. The five strongest X-ray diffraction lines are [d<sub>meas</sub>. in Å (I) (hkl)]: 3.915 (35) (100), 2.765 (100) (110), 1.953 (53) (200), 1.594 (30) (211), 1.380 (22) (220). The compositional features of isolueshite suggest that the mineral is a stabilised polymorph of NaNbO<sub>3</sub>. The name is for isometric habit and optical isotropism of the mineral, compared with the orthorhombic polymorph lueshite. Cotype samples are deposited in the Mining Museum of the Mining Institute, St. Petersburg, and in the Mineralogical Museum of St. Petersburg State University, Russia.

Key-words: new mineral, isolueshite (Na, La, Ca) (Nb, Ti)O<sub>3</sub>, lueshite, natroniobite, perovskite group, Khibina complex, Kola Peninsula.

# Introduction

The Khibina alkaline complex, Kola Peninsula, Russia, covering an area of 1327 sq. km is the largest body of nepheline syenites and allied rocks in the world. The complex emplaced into Archean granite gneisses and Proterozoic volcanic-sedimentary lithologies consists of (from the western contact inwards): umptektite and nepheline syenite, massive and trachytic khi-

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binites, foidolite series associated with poikilitic nepheline syenite (rischorrite), massive and trachytic foyaites, carbonatite (Sørensen, 1970; Kostyleva-Labuntsova *et al.*, 1978; Kogarko *et al.*, 1995). The rocks of the Khibina complex have been dated at  $362.4 \pm 4.5 - 377.3 \pm 3.9$  Ma (Kramm *et al.*, 1993).

Until recently, only two perovskite-group minerals were known to occur at Khibina: perovskite in ultrabasic xenoliths and foidolites (Shilin & Yanchenko, 1962; Shpachenko et al., 1990), and loparite-(Ce) in nepheline syenites, associated pegmatites and metasomatites (Kuznetsov, 1925; Tikhonenkova et al., 1982; Bel'kov et al., 1988; Chakhmouradian et al., 1995). In 1957, Tikhonenkov & Kazakova described "nioboloparite" as a new species (Tikhonenkov & Kazakova, 1957). Subsequently, "nioboloparites" have been found at several localities in the Khibina and Lovozero complexes, Kola Peninsula (Semenov, 1972; Shliukova & Unanova, 1972; Kostyleva-Labuntsova, 1978), and in the Schryburt Lake complex, Ontario, Canada (Platt, 1994). Neotype samples of Tikhonenkov & Kazakova's "nioboloparite" have been re-investigated by Mitchell et al. (1996). These authors have proved this mineral to be ordinary loparite-(Ce) with an average Nb<sub>2</sub>O<sub>5</sub> content of 11 wt.% and suggested that the name "nioboloparite" should be abandoned as a valid mineral name.

First samples of isolueshite were found by one of the authors (VYa) at the Kukisvumchorr underground apatite mine, southern Khibina, in 1991. The samples were preliminary studied by Mitchell *et al.* (1996) who classified the mineral as lanthanian lueshite on the basis of its composition. Subsequently undertaken single-crystal Xray analysis and optical investigation indicated that this mineral was a new mineral species which, unlike compositionally similar lueshite, had a cubic symmetry.

Isolueshite was named according to its isometric habit, optical isotropism and compositional similarity to the orthorhombic NaNbO<sub>3</sub> polymorph lueshite (Safiannikoff, 1959). Both the mineral and its name were approved by the Commission on New Minerals and Mineral Names, IMA (vote 95-024). Cotype samples are deposited in the Mining Museum of the Mining Institute, St. Petersburg, under catalogue number 3007, and in the Mineralogical Museum of St. Petersburg State University, Russia, under catalogue number 1/18271.



Fig. 1. Geological setting and zonation of isolueshitebearing hydrothermally altered pegmatite vein. Kukisvumchorr apatite deposit, south Khibina. 1 ijoliteurtite, 2 contact zone, 3 intermediate zone, 4 cavernous zone.

### Occurrence

Isolueshite occurs in a hydrothermally altered pegmatite vein (Fig. 1) cutting ijolite-urtite (1) at the Kukisvumchorr apatite deposit (southern part of the complex). There are three zones distinguished within the vein: a microcline-sodaliteaegirine zone with arfvedsonite and lamprophyllite as minor phases at the contact (2); an intermediate zone composed of natrolite, pectolite, lamprophyllite, astrophyllite and fersmanite (3); a series of cavities up to 0.5 m across with crystals and spherulites of natrolite and calcite (4). Isolueshite is found only in the contact zone as euhedral crystals and their intergrowths enclosed in microcline and sodalite. The crystals of isolueshite include scarce microlaths of microcline and isometric grains of Th-rich titaniumniobium oxide, probably pyrochlore.

# Physical and optical properties

Isolueshite crystals are a combination of cube and rhombic dodecahedron, and reach 0.3 mm in size. {110} faces are fine-striated parallel to the edges common with cube faces (Fig. 2a). The mineral is brownish-black with pale-yellow streak and adamantine lustre, brittle with uneven fracture. There is no evidence of the pseudocubic cleavage typical of lueshite and perovskite.



Fig. 2. Morphology and zonation of isolueshite. a - SEM photograph of a crystal. Scale bar is 0.2 mm; b - zonation pattern. Schematic drawing of a back-scattered electron image.

The microhardness (70-g indentor) is slightly higher on {110}, compared to {100}: 544-616 and 479-544, respectively. An average microhardness of 580 corresponds to 5.5 on the Mohs' scale. The measured density is 4.72(1) g/cm<sup>3</sup> (average of three measurements by microburette method); the calculated density is 4.69 g/cm<sup>3</sup> based on the empirical formula and the measured unit-cell parameters, Z = 1.

Isolueshite is optically isotropic in fine pieces. Under reflected light, the mineral is bluish with internal reddish-brown reflections. Reflectance values obtained as average of four measurements are given in Table 1. Refractive index (S-Se media) is 2.20(1) which is close to 2.22 calculated from reflectance values at 660-700 nm (redorange range of the visible spectrum).

Table 1. Reflectance values of isolueshite.

R, %	λ, nm
440	16.55
460	16.05
480	15.75
500	15.50
520	15.25
540	15.00
560	14.80
580	14.70
600	14.55
620	14.45
640	14.40
660	14.35
680	14.35
700	14.35

An infra-red absorption spectrum of the mineral was obtained on a Zeiss UR-20 spectrometer (KBr-pellet). Two major absorption bands at 415 cm<sup>-1</sup> and 600 cm<sup>-1</sup>, as well as a general spectrum pattern indicate correspondence of isolueshite to the perovskite group.

## **Chemical composition**

A preliminary study of the mineral in backscattered electrons has revealed its complex zonation (Mitchell *et al.*, 1996). There are four distinct zones within the crystal that significantly differ in composition; the zones are generally parallel to the {100} faces (Fig. 2b).

Compositions of the different zones were determined by wavelength dispersive method (WDS) using a Cameca SX-50 electron microprobe following the analytical scheme utilised by Mitchell & Vladykin (1993). Except LREEs, all elements were determined at an accelerating voltage of 15 kV and beam current 20 nA, the light rare earths at 20 kV and 40 nA, respectively. Standards used for the microprobe work are reported in Table 2.

Table 2 gives the representative chemical compositions and structural formulae of different zones within the crystal. The assignment of Th to the twelve-coordinated A-sites achieves better stoichiometry of the formulae and is corroborated by its ionic radius in a twelve-coordinated polyhedron (1.21 Å: Shannon, 1976), although the site preference for Th in Na and Nb-enriched

	1	2	3	4	
Na <sub>2</sub> O	13.65	12.82	12.05	12.28	
K₂O	0.07	0.06	0.09	0.04	
CaO	2.82	2.25	2.16	1.48	
SrO	2.03	2.02	1.66	1.42	
La₂O₃	5.17	7.80	7.08	7.83	
Ce <sub>2</sub> O <sub>3</sub>	3.12	5.07	5.08	7.44	
Pr <sub>2</sub> O <sub>3</sub>	0.15	0.20	0.21	0.45	
Nd <sub>2</sub> O <sub>3</sub>	0.18	0.33	0.47	0.82	
Sm <sub>2</sub> O <sub>3</sub>	n.d	n.d	n.d	0.03	
ThO₂	1.15	2.41	4.88	2.98	
FeO <sub>T</sub> *	0.02	0.03	n.d	0.02	
TiO₂	17.05	21.08	22.24	23.00	
Nb <sub>2</sub> O <sub>5</sub>	53.41	44.23	41.81	40.68	
Ta <sub>2</sub> O <sub>5</sub>	0.58	0.79	0.64	0.39	
Total	99.40	99.09	98.37	98.86	

Table 2. Compositions (wt.%) and structural formulae of isolueshite.

1  $(Na_{0.73} La_{0.05} Ce_{0.03} Ca_{0.08} Sr_{0.03} Th_{0.01})_{0.93} (Nb_{0.66} Ti_{0.35})_{1.01} O_{3.00}$ 

 $2 \hspace{0.1in} (Na_{0.70} \hspace{0.1in} La_{0.08} \hspace{0.1in} Ce_{0.05} \hspace{0.1in} Ca_{0.07} \hspace{0.1in} Sr_{0.03} \hspace{0.1in} Th_{0.02})_{0.95} \hspace{0.1in} (Nb_{0.56} \hspace{0.1in} Ti_{0.45} \hspace{0.1in} Ta_{0.01})_{1.02} \hspace{0.1in} O_{3.00}$ 

3  $(Na_{0.66} La_{0.07} Ce_{0.05} Ca_{0.07} Sr_{0.03} Th_{0.03})_{0.91} (Nb_{0.54} Ti_{0.48})_{1.02} O_{3.00}$ 

 $(Na_{0.68} La_{0.08} Ce_{0.08} Nd_{0.01} Ca_{0.05} Sr_{0.02} Th_{0.02})_{0.94} (Nb_{0.52} Ti_{0.49})_{1.01} O_{3.00}$ 

 $5 \hspace{0.2cm} (Na_{0.68} \hspace{0.2cm} La_{0.08} \hspace{0.2cm} Ce_{0.07} \hspace{0.2cm} Nd_{0.01} \hspace{0.2cm} Ca_{0.06} \hspace{0.2cm} Sr_{0.02} \hspace{0.2cm} Th_{0.02})_{0.94} \hspace{0.2cm} (Nb_{0.53} \hspace{0.2cm} Ti_{0.48})_{1.01} \hspace{0.2cm} O_{3.00}$ 

1 inner core, 2 outer core, 3 inner rim, 4 outer rim, 5 empirical formula. \* Total Fe as FeO. n.d ≈ not detected. All structural formulae calculated on the basis of 3 atoms of oxygen. Standards: albite (Na), almandine (Fe), diopside (Ca), microlite (Ta), monazite (Ce), olivine (Mg), orthoclase (K), spessartine (Mn), thorite (Th), witherite (Ba), metallic Pb, SrTiO<sub>2</sub> (Sr, Ti), LaVO<sub>4</sub> (La), ZrO<sub>2</sub>, Nb<sub>2</sub>O<sub>5</sub> and REE-bearing glasses (Pr, Nd, Sm) (Drake & Weill, 1972). Ba, Pb, Mg and Zr were sought, but not detected.

perovskite-type compounds is unknown. From Table 2, it is evident that isolueshite has the following compositional features:

i) Nb dominates over Ti in the six-coordinated B-sites.

ii) Na dominates over LREEs, Ca and other A-cations. It is noteworthy that La, not Ce, is a major element among REEs in isolueshite. The data available from the literature show that all previously analysed perovskite-group minerals are Ce-dominant species.

For instance, Ce/La ratio in loparites-(Ce) ranges between 1.2 and 2.3 (Chakhmouradian *et al.*, 1995; Haggerty & Mariano, 1983; Khomy-akov, 1972; Kozyreva *et al.*, 1991; Subbotina *et al.*, 1991). According to 18 microprobe determinations, the Ce/La ratio in isolueshite gradually increases from 0.5-0.6 at the core to 1.0 at the outer rim.

iii) Cation deficiency at the A-sites, which implies that some of the twelve-coordinated sites in the "rigid" framework of (Nb,Ti)O<sub>6</sub> are vacant. This phenomenon is well-known for synthetic tungsten bronzes  $M_xWO_3$  (0 < x < 1, M = K, Na, Ba, *etc.*) (Mitchell, 1996).

iv) The mineral compositionally evolves through Ti, Ce, Pr and Nd-enrichment, coupled with

depletion in Ca, Sr and Nb from the core toward the rim.

The ternary system lueshite NaNbO<sub>3</sub> - perovskite CaTiO<sub>3</sub> - NaLaTi<sub>2</sub>O<sub>6</sub> was chosen for graphic representation of the compositional evolution of isolueshite. NaLaTi<sub>2</sub>O<sub>6</sub> as a lanthanium analogue of loparite-(Ce) has not been found in nature, but has been synthesised and shown to possess the perovskite structure (Mitchell, 1996). Fig. 3 depicts the core-to-rim zonation trend observed in isolueshite. It is essentially from La-Ca-rich lueshite to La-rich lueshite nearly parallel to the NaNbO<sub>3</sub>-NaLaTi<sub>2</sub>O<sub>6</sub> join. Although all composition points of isolueshite fall within the lueshite field of the ternary plot, X-ray crystallography findings (see below) allow the distinction of this mineral as a new species.

The empirical formula of isolueshite (Table 2) was calculated on the basis of relative volume proportions occupied by compositionally different zones. The obtained empirical formula is very close to structural formula of the fourth zone occupying more than 70 % of crystal's volume (see Fig. 2b). The Gladstone-Dale relationship computed from the empirical formula (Mandarino, 1976 and 1981) is 0.010 (excellent correspondence).

Isolueshite, new perovskite-group mineral



Fig. 3. Compositions (mol.%) of isolueshite (1), lueshite (2) and loparites-(Ce) (3) in the ternary systems NaNbO<sub>3</sub>-CaTiO<sub>3</sub>-NaLaTi<sub>2</sub>O<sub>6</sub> and NaNbO<sub>3</sub>-CaTiO<sub>3</sub>-NaCeTi<sub>2</sub>O<sub>6</sub>. Data on lueshite from Mitchell (1996); data on loparites-(Ce) from Mitchell & Chakhmouradian (1996).

# X-ray crystallography

The X-ray diffraction (XRD) pattern of isolueshite was obtained on a DRON-2.0 diffractometer at a goniometer rotation rate of 0.25° per minute ( $CuK\alpha$  radiation, Ge internal standard). The XRD pattern of isolueshite is very similar to that of perovskite-type compounds with ideal cubic structure, for instance SrTiO<sub>3</sub> (ASTM file card 5-0636). Unlike the XRD pattern of orthorhombic lueshite (Table 3), that of isolueshite lacks weak reflections (e.g.  $d \approx 3.80; 3.12; 2.47$ ) and splittings of some strong lines (e.g.  $d \approx 3.88$ -3.91; 2.75-2.78). The unit-cell dimensions of isolueshite were refined from the XRD pattern by the least-squares method using the domestic PARAM program for PC (Table 3). Single-crystal X-ray studies by oscillating-crystal (camera RKV-86) and de Jong-Bouman (camera KFOR) methods confirmed the cubic symmetry of isolueshite (diffraction symbol m3mP). The space group of the mineral cannot be defined unequivocally because of the absences. By analogy with other cubic perovskite-type compounds, we suggest the space group *Pm3m* corresponding to aristotype structure (Megaw, 1973). Further studies of the isolueshite structure are being undertaken by H. R. Wenk (University of California at Berkeley).

#### Discussion

The above compositional and structural data indicate that isolueshite is a cubic polymorph of sodium niobate. It is well-known that cubic NaNbO<sub>3</sub> stable above 640°C undergoes several phase transitions with decreasing temperature (Ahtee *et al.*, 1972; Denoyer *et al.*, 1971; Glazer & Megaw, 1972; Ismailzade, 1963; Solov'ev *et al.*, 1961). The P-phase stable at room temperature is orthorhombic with space group *Pbcm* (Sakowski-Cowley *et al.*, 1969) or *Pbma* (Glazer, 1972). At the same time, the stable roomtemperature structural form of NaNbO<sub>3</sub> with 2.5 mol.% KNbO<sub>3</sub> is not the P-phase, but the Q-

Isolueshite						Lues	hite*			Natro	niobite <sup>#</sup>
hkl	I.	<b>d</b> <sub>meas</sub>	d <sub>calc</sub>	hkl	ŧ	d	hki	1	d	1	d
100	35	3.915	3.9110	101	90	3.912	143	20	1.5894	2	4.8
110	100	2.765	2.7655	040	45	3.882	191	1	1.5780	4	3.79
				111	1	3.797	203, 312	1	1.5314	2	3.36
200	53	1.953	1.9555	131	<1	3.122	182, 213	1	1.5252	3	3.29
				200	25	2.785	0.10.1	<1	1.4947	9	3.06
210	8	1.747	1.7491	141,002	100	2.754	400	3	1.3923	10	2.97
211	30	1.594	1.5967	102	1	2.468	371, 282	13	1.3779	2	2.79
220	22	1.380	1.3827	211, 230	1	2.453	253	8	1.3745	3	2.69
				112	1	2.435	411, 430	<1	1.3445	1	2.60
221	1	1.295	1.3037	221	1	2.366	104	<1	1.3362	1	2.47
300			1.3037	122	1	2.351	124, 2.10.1	<1	1.3164	3	2.39
310	7	1.234	1.2368	061	1	2.342	440	1	1.3105	1	2.30
				240	1	2.263	381	4	1.3032	2	2.25
				042	2	2.245	044, 183	5	1.2965	1	2.04
222	2	1.128	1.1290	241	<1	2.093	0.12.0, 134	3	1.2935	1	1.99
				202	25	1.9574	333	<1	1.2649	3	1.93
321	5	1.042	1.0453	080, 251	16	1.9400	402	2	1.2424	5	1.89
				023, 162	1	1.7857	412	3	1.2385	1	1.87
				301	7	1.7591	343	3	1.2369	2	1.76
				311, 242	12	1.7478	204	3	1.2336	6	1.72
				103	14	1.7432	1.12.1	5	1.2283	8	1.60
				181	16	1.7385	442	<1	1.1831	4	1.59
				331	1	1.6652	244	1	1.1757	4	1.544
				043	1	1.6593	0.12.2	1	1.1706	4	1.523
				341	11	1.6018	480	1	1.1311	2	1.481
_			(0)								
a <sub>0</sub> , /	. Δ	3.911	(3)			5 569	87(5)				
h	h				15.50	23(2)					
C	Ā					5 504	7(12)				
V, A	3	59.8	(1)			0.004	( ( <b>Z</b> )				

Table 3. Comparison between X-ray powder diffraction data of isolueshite, lueshite and natroniobite.

\* ASTM 33-1270. \* Kukharenko et al. (1965).

phase (Wells & Megaw, 1961). Transitions in which structural modifications are induced by changes in composition rather than by thermody-

namic factors are termed "stabilised polymorphism" and are well-known for naturally occuring TiO<sub>2</sub> and ZrO<sub>2</sub> (Smirnova & Belov, 1969).

Table 4. Morphology, physical and optical properties of isolueshite, lueshite and natroniobite.

	Isolueshite	Lueshite*	Natroniobite <sup>#</sup>	
Morphology	Cube + mombic dodecahedron	Pseudocube	Pseudomorphs after perovskite and pyrochlore	
Colour	brownish-black	black	yellow to brownish-black	
Anisotropism	isotropic	anisotropic	anisotropic	
Refractive	2.20(1)	2.30	2.10-2.24	
Mohs' hardness	5.5	5.5	5.5-6	
Microhardness	479-616	-	-	
Density	4.72(1)	4.44	4.40	
Cleavage	none	pseudocubic	none	

\* Safiannikoff (1959). \* Kukharenko et al. (1965).

Significant amounts of LREE and Ti in the isolueshite suggest that this mineral is a LREE-Ti-stabilised polymorph of NaNbO<sub>3</sub>. The other natural NaNbO<sub>3</sub> polymorph is lueshite first described from the Lueshe carbonatite complex, Zaire (Safiannikoff, 1959). This author has determined for lueshite the space group *P*222<sub>1</sub> which differs from that of synthetic NaNbO<sub>3</sub> at room temperature (see above). The recently reinvestigated composition of lueshite is close to theoretical: (Na<sub>0.855</sub> Ca<sub>0.031</sub> Ce<sub>0.011</sub> La<sub>0.005</sub> Nd<sub>0.003</sub>) Pr<sub>0.002</sub> Th<sub>0.003</sub>)<sub>0.910</sub> (Nb<sub>0.959</sub> Ti<sub>0.049</sub> Ta<sub>0.003</sub>)<sub>1.011</sub> O<sub>3</sub> (Mitchell, 1996, Table 5).

In most recently published glossaries of mineral species, natroniobite is considered as a monoclinic polymorph of NaNbO3 (e.g. Fleisher & Mandarino, 1995). This mineral has been discovered in a number of carbonatite complexes at the Kola Peninsula and then described in detail by Kukharenko et al. (1965). The empirical formula of natroniobite NaNb2O5OH and the close resemblance between X-ray diffraction patterns of natroniobite and fersmite CaNb2O6 suggest that both minerals are isostructural (Kukharenko et al., 1965). Therefore, natroniobite should be regarded as a sodium-analogue of fersmite rather than a monoclinic polymorph of NaNbO<sub>3</sub>. The X-ray diffraction data of isolueshite, synthetic lueshite and natroniobite are compared in Table 3. Morphology, physical and optical properties of isolueshite, naturally occuring lueshite and natroniobite are given in Table 4.

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