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Nos 20–21

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- 20 On the mineralogy and paragenesis of tugtupite $\text{Na}_3\text{Al}_2\text{Be}_2\text{Si}_8\text{O}_{24}(\text{Cl},\text{S})_2$ from the Ilimaussaq alkaline intrusion, South Greenland..... H. SØRENSEN, M. DANØ and O. V. PETERSEN.
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THE COLOUR AND LUMINESCENCE OF
TUGTUPITE (BERYLLOSODALITE) FROM
ILÍMAUSSAQ, SOUTH GREENLAND

CONTRIBUTION TO THE MINERALOGY OF ILÍMAUSSAQ, No. 21

BY

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WITH 2 FIGURES AND 3 TABLES IN THE TEXT

С РУССКИМ РЕЗЮМЕ

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1971

Abstract

Tugtupite, $\text{Na}_4[\text{BeAlSi}_4\text{O}_{12}]\text{Cl}$, is a mineral with bright pink colour and yellow-orange UV-luminescence. The visible region of the spectral absorption curves and the luminescence spectrum of tugtupite from the Ilímaussaq alkaline massif (South Greenland) were studied. Calculated and experimental values of vibrational frequencies of different molecular ions were compared, and it was established that the luminescence of tugtupite is caused by S_2^- molecular ions occupying the position of Cl ions in the crystal structure. These ions are also the cause of the colour of tugtupite, probably in combination with other, thermally less stable, radiation centres.

РЕЗЮМЕ

Тугтупит $\text{Na}_4[\text{BeAlSi}_4\text{O}_{12}]\text{Cl}$ — минерал, имеющий ярко-розовую окраску и желто-оранжевую УФ-люминесценцию. Были изучены кривые спектрального поглощения в видимой области и кривая спектра люминесценции образцов тугтупита из пегматитов щелочного массива Илимауссак (Южная Гренландия).

На основе сравнения рассчитанных и экспериментальных величин колебательных частот различных молекулярных ионов было установлено, что причиной люминесценции тугтупита являются молекулярные ионы S_2^- , расположенные в его структуре на местах ионов Cl. Они же обуславливают окраску тугтупита, хотя в отношении последней не исключается роль и других, термически менее устойчивых, радиационных центров.

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Introduction

The mineral tugtupite (beryllosodalite) has been found in the Ilímausaq (South Greenland) and Lovozero (Kola Peninsula) alkaline intrusions (SØRENSEN, 1960; SØRENSEN, DANØ & PETERSEN, in press; SEMENOV & BYKOVA, 1960).

It belongs to the beryllo-alumino-tectosilicates and is isotypical with the sodalite group minerals. It is tetragonal, pseudocubic. Density – 2.30; hardness – $5\frac{1}{2}$. Cleavage bipyramidal distinct. The mineral is uniaxial (or nearly so) positive, $n_o = 1.496$ and $n_e = 1.502$ (DANØ, 1966).

As is characteristic of all mineral species of the feldspathoid group, tugtupite has a distinct coloration and luminescence. It is bright crimson and has an orange luminescence. The nature of these optical properties is investigated in this paper.

Chemical composition and structure

With respect to chemistry tugtupite differs from sodalite in that two atoms of Al are substituted by Be and Si, giving the following formula: $\text{Na}_4(\text{BeAlSi}_4\text{O}_{12})\text{Cl}$. DANØ (1966) has shown that the Be and Al atoms are ordered in the framework, BeO_4 and AlO_4 tetrahedrons being located on fourfold axes, which decreases the mineral symmetry from cubic, as in sodalite (PAULING, 1930), to tetragonal (pseudocubic) with the parameters $a = 8.583$ and $c = 8.817$ (DANØ, 1966).

Each of the four oxygen atoms in the BeO_4 and AlO_4 tetrahedrons is linked only with Si atoms (common for two tetrahedrons), and therefore these tetrahedrons are of regular form. One third of the SiO_4 tetrahedrons in the tugtupite structure are entirely bound to analogous tetrahedrons, and the other two thirds have apices in common with two SiO_4 tetrahedrons and with AlO_4 and BeO_4 tetrahedrons, which results in a rather strong distortion ($\text{Si-O} = 1.566\text{--}1.646$).

The Na atoms are in the framework cavities in fourfold coordination and are surrounded by three atoms of O and one atom of Cl. The Cl atoms are surrounded by four Na atoms. Each of the oxygen atoms bound to Be is unsaturated with respect to valency and has a half excess charge, which, taking into account a resonance displacement of electron

Table 1. *Chemical analyses of tugtupite (beryllosodalite).*

	Weight percent	
	Tugtupite from Ilimaussaq	Beryllosodalite from Lovozero
SiO ₂	51,58	50,45
Al ₂ O ₃	11,15	12,56
Ga ₂ O ₃	Not determ.	0,043
Fe ₂ O ₃	Traces	Not determ.
BeO.....	5,40	5,30
MgO.....	0,20	Not determ.
CaO.....	Not determ.	0,50
Na ₂ O.....	25,52	23,26
K ₂ O.....	0,12	0,40
H ₂ O.....	0,03	1,51
S.....	0,33	Not determ.
	101,61	101,56
- O = Cl ₂	1,64	1,40
- O = S.....	0,16	-
Total.....	99,81	100,16
Analyst.....	M. MOURITZEN (1960)	A. V. БЫКОВА (1960)

clouds enables two of four O atoms to have one localized electron for short periods. For the O atoms surrounding Al such electron localization is possible for only one in four.

In the normal stoichiometrical composition excess negative charges in the BeO₄ and AlO₄ tetrahedrons ($\frac{1}{4}$ Cl + $\frac{1}{4}$ O_{Al} + $\frac{1}{2}$ O_{Be}) are strictly compensated by the positive Na⁺ charges. However, in displacing or removing the weakly bonded Na and Cl atoms from their positions in the structure, favourable conditions are created for localization of electrons that can be easily excited.

Heterovalent isomorphous substitution of atoms is an essential generator of defects in feldspathoid framework structures. The most common example of this is the substitution of Cl by S atoms, as in S-sodalite known as hackmanite (VOROBIÉVA, 1946). As can be seen from the chemical analysis (table 1), the content of sulphur in tugtupite is considerable. But it is difficult to say a priori whether it is represented in the structure by simple ions S⁻² or by molecular ions such as S₂⁻² or S₂⁻ (SCHULMANN & KIRK, 1964). In both cases the location of S atoms in the positions of the Cl atoms results in the appearance of local disturbances of the valency balance. This may manifest itself either in the presence of negative vacancies or in the appearance of excess negative charges on the sulphur ions.

The colour of tugtupite

The optical absorption spectra of tugtupite were measured by means of the spectrophotometer "SF-4A" with a special device for examination of powdered samples.

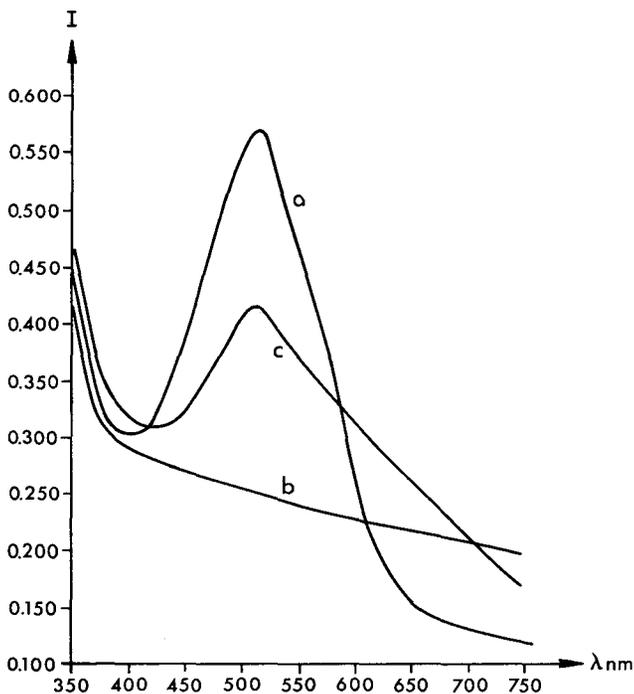


Fig. 1. The spectral absorption curves of tugtupite in the region 350–700 nm: a: naturally coloured sample; b: decolourized by heating at 450° C; c: irradiated with X-rays.

The bright pink (crimson) colour of tugtupite is conditioned by a wide band of light absorption in the visible region within the range 440–600 nm with the maximum at 510 nm (fig. 1, curve *a*). The optical density of the sample is considerably lower in the red region (600–750 nm) of the spectrum than at shorter wave lengths (350–600 nm).

The sample was completely decolourized and became white after heating to 450° C. The optical density of the heated sample was preserved in the ultraviolet region, but decreased gradually with increasing wave length in the visible region of the spectrum (fig. 1, curve *b*).

A sample decolourized by heating was exposed to X-rays (tube "BSV-2", Mo-radiation, 40 kV, 10 mA). After irradiation for 2 hours the sample acquired a pink colour. The absorption band within the range

450–600 nm (with the maximum at 510 nm), which is analogous to that of the naturally coloured sample, was partially restored, though it did not reach its original intensity (fig. 1, curve c). When the dose of irradiation was increased, the colour was intensified. The artificial colour of tugtupite obtained by irradiation is unstable and disappears completely after exposure to day light for 2–3 hours. This indicates that the colour centres obtained in this way are unstable. A similar phenomenon can also be observed on naturally coloured S-containing sodalite (hackmanite) from pegmatites of the alkaline rocks of the Kola Peninsula (BORGSTRÖM, 1901; VOROBIJEVA, 1946).

The luminescence of tugtupite

When investigating samples of tugtupite in ultraviolet light a bright yellow-orange luminescence was observed. The spectrum (fig. 2) was recorded on a special spectrophotometer which made it possible to register

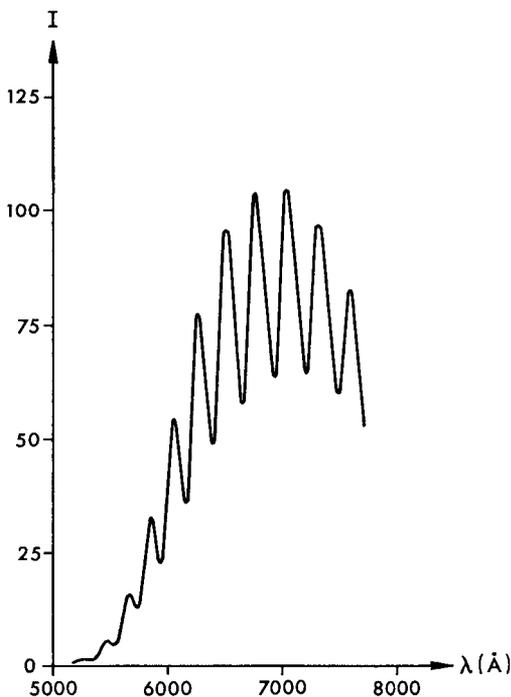


Fig. 2. The luminescence spectrum of tugtupite ($T = 77^\circ \text{K}$).

luminescence within the range 300–800 nm. Luminescence was produced by the line at 365 nm of the mercury spectrum; the spectra were photographed at the temperature of liquid nitrogen (77°K). The luminescence of the samples did not disappear even after heating to 900°C , and

the spectrum of the heated samples is similar to that of the non-heated ones.

The luminescence spectrum of tugtupite presents a wide band consisting of 11 narrow equispaced bands, the spectral positions of which are given in table 3.

Table 2. *Vibrational frequencies of the molecular ions of oxygen and sulphur*

Molecular ions of oxygen	Δv_{av} , cm ⁻¹	Author	Molecular ions of sulphur	Δv_{av} , cm ⁻¹	Author
O ₂ ⁺	1876	HERZBERG, 1950	S ₂ ⁰	726	HERZBERG, 1950
O ₂ ⁰	1580	HERZBERG, 1950	S ₂ ⁻ in KCl	587	ROLFE et al. 1961
O ₂ ⁻	1260±70	SCHULMANN & KIRK, 1964	S ₂ ⁻ in KBr	580	ROLFE et al. 1961
O ₂ ⁻ in NaCl	975	SCHULMANN & KIRK, 1964	S ₂ ⁻ in Na ₂ SO ₄	567	ROLFE et al., 1961
O ₂ ⁻ in KCl	980	SCHULMANN & KIRK, 1964	S ₂ ⁻ in CaSO ₄	600	Data of authors
O ₂ ⁻ in KBr	962	SCHULMANN & KIRK, 1964	S ₂ ⁻ in BaSO ₄	620	

Similar spectra are typical for absorption and radiation of various molecular ions, for instance the diatomic molecules H₂, F₂, O₂, S₂ (HERZBERG, 1950). Molecules, as well as atoms, have discrete energy levels – electronic, vibrational and rotational – the energetic positions of which are different in the spectra. In the ultraviolet and visible regions electronic bands are usually observed associated with transitions between different states of electron shells of molecules. A definite set of vibrational nuclear energy levels corresponding to each state of the electron shells and radiation (or absorption) of the molecule will be presented by an electron-vibrational spectrum; vibrational processes complicate the structure of the electronic band.

Discussion

On the basis of what has been said, one can draw the conclusion that the luminescence spectrum of tugtupite is of electron-vibrational nature and due to the presence of molecular ions in the crystal structure. The distances (Δv) between the narrow bands of the spectrum correspond to the distances between the vibrational sublevels of the basic state of molecular ions (HERZBERG, 1950; ROLFE, LIPSETT & KING, 1961).

The luminescence centres can be unequivocally identified by the EPR method, but in our case this method is not suitable because of the cryptocrystalline nature of the object under study. Nevertheless, on the basis of the known experimental data (PRINGSHEIM, 1949; SCHULMANN & KIRK, 1964), one may conclude that molecular ions of oxygen and sulphur can be the luminescence centres in tugtupite.

Each of such ions is characterized by a definite average vibrational frequency (Δv_{av}) depending mainly on the electronic structure of the ion and, to a lesser extent, on the crystal field of the compound in which this ion is present. Average vibrational frequencies of molecular ions of oxygen and sulphur are presented in table 2.

Table 3. *Frequency characteristic of the luminescence spectrum of tugtupite*

Number of band	ν, cm^{-1}	$\Delta\nu, \text{cm}^{-1}$	I (%)
1.....	18868	620	1,4
2.....	18248	580	5,2
3.....	17668	574	15,2
4.....	17094	565	30,4
5.....	16529	529	51,9
6.....	16000	592	74,3
7.....	15408	593	91,0
8.....	14815	570	99,0
9.....	14245	547	100,0
10.....	13698	506	92,4
11.....	13192		79,0

$\Delta v_{av} = 568$

$\Delta v_{av} = 568 \text{ cm}^{-1}$ (see table 3) of tugtupite calculated from the luminescence spectrum coincides with the value of $\Delta\nu$ for the molecular ion of S_2^- . The luminescence of the studied samples may therefore be associated with this ion. Radiational transitions in the ion S_2^- take place from one of the vibrational sublevels of the excited state to the vibrational sublevels of the basic state $2_{\pi_{3/2}}$.

The temperature stability of the tugtupite luminescence should be noted. This gives reason to suppose that the molecular ion S_2^- is almost as stable in the tugtupite structure as ionic S in lazurite. The difference here seems to be purely quantitative. In the latter mineral atoms of S predominate. Their action is thus more concentrated and, consequently, the position is more stable, which is particularly expressed in the fact that its colour cannot be wiped out at the highest temperatures (VORO-BIEVA, 1946).

It is obvious that the crimson colour of tugtupite is due not only to the molecular ions S_2^- , which are the cause of its luminescence, but also to still other, thermically less stable, radiation centres, for example $(SO_4)_2^-$, as is established for ussingite (POVARENNYKH, PLATONOV & BELICHENKO, 1970).

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