

Optical Properties of Natural and Synthetic Beryl Crystals

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Abstract. The results of investigation of photoluminescence and UV-Visible absorption spectra of natural beryl crystals from Ural Mountains before and after fast neutron irradiation and synthetic crystal grown in Belarus and Russia are presented. Photoluminescence (PL) spectra of synthetic beryl crystals contain a broad band with maxima 740 nm excited both by UV light ($\lambda_{\text{ex}} = 260 \text{ nm}, 271 \text{ nm}$) and laser excitation ($\lambda_{\text{ex}} = 263 \text{ nm}$). This band is connected with Fe^{2+} ions. The temperature lowering down to 8 K leads to appearance of narrow lines in the 680 - 720 nm regions. Emission lines observed in the luminescence spectra are connected with electron transition ${}^2E_g \rightarrow {}^4A_{2g}$ of the Cr^{3+} ions: R-lines (682.5 nm) arise from isolated Cr^{3+} ions occupying Al^{3+} sites; N-lines (691, 698, 703, 706 and 711 nm) arise from several types of exchange-coupled pairs of Cr^{3+} ions occupying first, second and third nearest and related neighbour Al^{3+} sites. It is shown that the absorption bands in the 690-580 nm region of natural pale blue beryl crystals caused by neutron irradiation belong to a complex center, which consists of Cr^{3+} ions and radiation defect - F or F^- center. Presence of Fe^{2+} ions contributes to the persistence of the complex defect.

1. Introduction

Beryl ($\text{Be}_3\text{Al}_2\text{Si}_6\text{O}_{18}$) is a ring silicate with a hexagonal structure, space group $\text{P6}/\text{mcc} \equiv \text{D}_{6h}^2$ [1, 2], in which Al^{3+} ions are located in octahedral coordination, and Si^{4+} and Be^{2+} ions - in tetrahedral coordination. The point symmetry of Si, Be and Al sites is C_s , D_2 and D_3 , respectively. The dominant structural units are rings of Si_6O_{18} composition. The Si_6O_{18} rings lay one above the other along the c-axis forming intercommunicating channels of quite large dimensions. The colour of beryl $\text{Be}_3\text{Al}_2\text{Si}_6\text{O}_{18}$ is usually determined by its Fe^{2+} and Fe^{3+} content. The golden yellow colour is attributed to Fe^{3+} ions [3]. Presence of Fe^{2+} produces pale blue color. If Fe^{2+} and Fe^{3+} are present simultaneously, the color of crystal is dark blue. Green color in iron-containing beryl usually results from a mixture of blue and yellow components. Green color can also come from Cr^{3+} as it is found in various emeralds [4]. Beryl is naturally transparent; however inclusions and impurities may make it opaque.

Natural and synthetic minerals of beryl are used not only as gemstone but have also practical industrial application. Beryl crystals find application as laser and dosimetry materials [5, 6]. Small amount of impurities and structural defects have a significant effect on the physical properties of crystals, chemical and radiation resistance of products and devices manufactured on the basis of beryl crystals. Therefore it is important to estimate the present material defects and their effect on properties of material. Optical absorption (OA) spectra in the visible range were subject of several authors' reports on beryl [7-12].

The paper presents study of optical properties of natural crystals before and after fast neutron irradiation and synthetic beryl crystals that may provide a way to address the physical processes responsible for the creation of the colour centres.



2. Materials and Methods

Natural and synthetic beryl $\text{Be}_3\text{Al}_2\text{Si}_6\text{O}_{18}$ samples were obtained from different sources: natural crystals from Ural Mountains (Beryl Natural green-1, 2 and 3 and Beryl Pale blue) and synthetic crystals grown in Belarus (Beryl M) and Russia (Beryl Flux and Beryl Cr 0.1%). The samples thickness was in the range of 0.5–2.15 mm for natural crystals and in the range of 0.475 to 5.75 mm for synthetic crystals.

The neutron irradiation was carried out in the Latvian 5 MW water-water research reactor. The fluence of fast neutrons with energy > 0.1 MeV was in the range $10^{14} - 10^{16} \text{ cm}^{-2}$. A cadmium filter was used for thermal neutrons absorption. During the neutron irradiation the samples temperature did not exceed 313 K.

A conventional experimental setup was used for measurements of photoluminescence (PL). Two types of UV light sources were used in the excitation channel of the setup: 1) a solid state laser DTL-389QT ($\lambda = 263$ nm), with nominal pulse energy 4.7 mJ at 1 kHz, and 2) a deuterium lamp LDD-400 with an attached grating monochromator MDR-2. The PL signal was analysed by Shamrock monochromator SR-303i-B and detected by a CCD camera DV420A-BU2.

Absorption spectra were measured either with a "Specord 210" (Analytikjena) double-beam spectrophotometer (190–1100 nm operation range) or with a "Specord M-40" two-beam spectrometer (200–900 nm operating range). Optical measurements before and after irradiation were carried out at room temperature (RT). For photoluminescence measurements at low temperatures a sample was put into refrigerator "Janis" providing temperatures from 8 to 300 K.

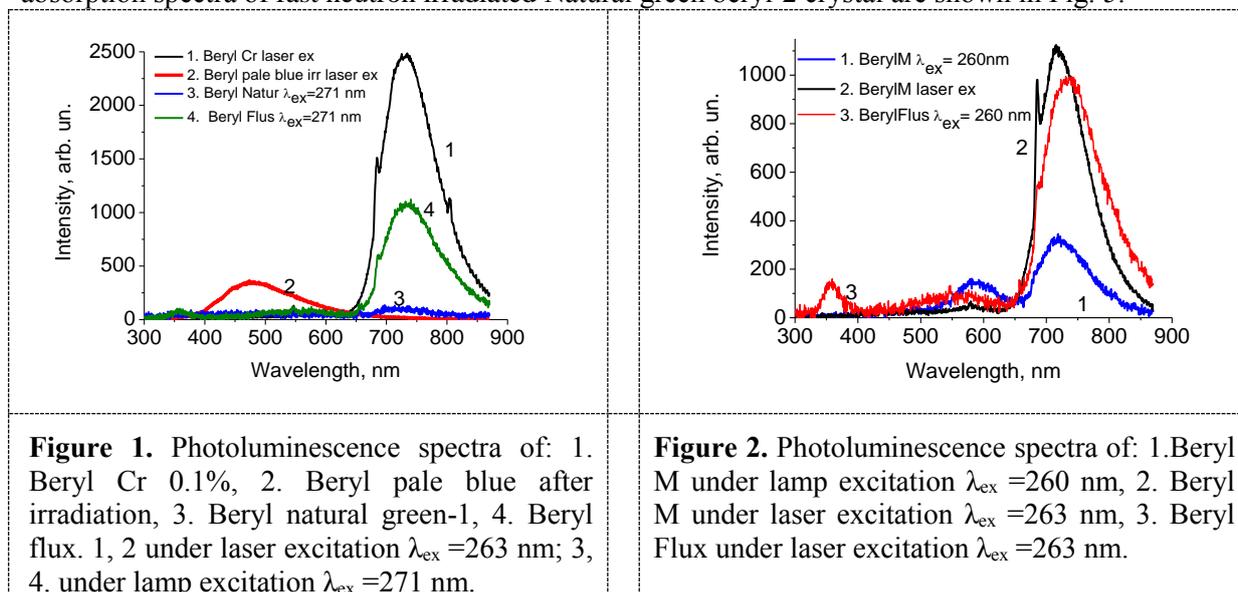
3. Results and Discussion

Fig. 1 and 2 show the photoluminescence spectra for different beryl crystals at various types of excitation. Photoluminescence spectra of beryl crystals contain a broad band with maxima 740 nm at UV light ($\lambda_{\text{ex}} = 260$ nm, 271 nm) as well as at laser excitation ($\lambda_{\text{ex}} = 263$ nm). This wide band is connected with Fe^{2+} ions [13]. When beryl crystals are exposed to UV light from the lamp, samples show a weak luminescence (Fig. 1, curve 3, 4 and Fig. 2, curve 1, 3), use of more intense laser excitation allows additional observation of narrow line at 685 nm. The photoluminescence spectra of "Beryl Flux" at $\lambda_{\text{ex}} = 260$ nm and different temperatures are given in Fig. 3. The temperature lowering down to 8 K leads to appearance of narrow lines in the region from 680 to 720 nm. Some zero-phonon lines were observed in the electron transition ${}^2E_g \rightarrow {}^4A_{2g}$ region of the Cr^{3+} ions: R-lines (682.5 nm) arising from isolated Cr^{3+} ions occupying Al^{3+} sites; N-lines (691, 698, 703, 706 and 711 nm) arising from several types of exchange-coupled pairs of Cr^{3+} ions occupying first, second and third nearest and related neighbour Al^{3+} sites [14]. Moreover in the photoluminescence spectra at low temperature there appears a band with maxima at 525 nm, its intensity increases with temperature decrease, which possibly could be explained by charge exchange between impurity ions [15]. PL measurements demonstrate that all studied beryl samples contain emission bands due to the presence of iron and chromium ions.

Besides the iron and chromium induced bands in PL spectra there are also additional bands observed in beryl samples. Excitation with light 260 nm leads to the appearance of 580 nm band in crystal "Beryl M" (Fig. 2, curve 1) and 355 and 560 nm bands in crystal "Beryl Flux" (Fig. 2, curve 3). The irradiated by fast neutron $\Phi = 10^{14} \text{ cm}^{-2}$ "Beryl Pale blue" crystal excited by the laser shows a wide band with maxima 480 nm (Fig. 1, curve 2). This band probably is connected with peroxy-radical similar to irradiated topaz crystals [16].

The absorption spectra of beryl single crystals are given in Fig. 4. The chromium containing beryl crystals spectra is characterized by two broad bands near 430 and 600 nm as well as by sharp R-lines (Fig. 4, curve 1, 3, 4). The observed absorption bands are ascribed to the electronic transitions of chromium ion: 630 nm transition ${}^4A_{2g}(F) \rightarrow {}^4T_{2g}(F)$ and 431 nm transition ${}^4A_{2g}(F) \rightarrow {}^4T_{1g}(F)$. The optical absorption band at 315–326 nm is caused by charge transfer from O^{2-} to Fe^{3+} in the tetrahedral Be^{2+} site [17]. The wide absorption band with peak in the near-infrared range at 813 nm is observed in natural beryl spectra (Fig. 4, curve 2). The band is generally ascribed to internal electron transition of

${}^5T_2 ({}^5D) \rightarrow {}^5E ({}^5D)$ of Fe^{2+} ions localized in octahedral aluminium sites of beryl [18-21]. The absorption spectra of fast neutron irradiated Natural green beryl-2 crystal are shown in Fig. 5.



Irradiation produces additional bands with maxima: 286, 370, 500 and 667 nm (Fig.5, curve 3). Most probably these bands are due to anion intrinsic defects (the F^+ , F , F_2 , F_2^+ and F_2^{2+} centers) similar to those observed in Al_2O_3 [22, 23]. The absorption spectra of natural pale blue beryl crystals before and after fast neutron irradiation $\Phi = 10^{16} \text{cm}^{-2}$ are given in Fig. 6. Prior to irradiation there were no absorption bands associated with electronic transitions of chromium ions ${}^4A_{2g}(F) \rightarrow {}^4T_{2g}(F)$ (630 nm) and ${}^4A_{2g}(F) \rightarrow {}^4T_{1g}(F)$ (431 nm). Absorption spectra contain only the band 813 nm associated with Fe^{2+} ions. After the impact of fast neutrons the intensity of 813 nm band is reduced and the absorption edge is shifted due to appearance of an intense absorption band in the UV region. Besides, after irradiation there appear the additional bands with maxima 690, 645.9, 628.1, 606.2 and 588.7 nm (Fig. 6, curve 3). The crystal color is changed from pale blue to light green.

The so called "Maxixe" and "Maxixe-type" color centers observed at 600-700 nm were previously reported in paper [24-26]. Irradiation produces radicals NO_3^0 and CO_3^- , which seem to be related to blue colour in beryl, but crystals quickly lose colour after irradiation. The "nonfading" specimen examined in report [27] had not lost all of its colour over several years storage on a desk.

Green colour of beryl crystals caused by irradiation may be associated with changes in the valence state of iron and chromium ions. The Fe^{3+} impurity ion has the same valence as a substituted Al^{3+} ion. The Fe^{3+} impurity ions prefer to stay in the octahedral Al^{3+} sites in order to maintain the local charge neutrality of the beryl crystal. Consequently, the Fe^{2+} impurity ions are oxidized into the Fe^{3+} state. Possible reaction is: $Fe^{2+} \rightarrow Fe^{3+} + e^-$; $Fe^{2+} + V \rightarrow Fe^{3+} + X_s^-$, X_s^- being the constituent anions or radicals in regular lattice of beryl crystal.

Cr^{3+} impurity ions occupy only octahedral Al^{3+} sites in beryl crystal. Before the irradiation there is no absorption band corresponding to the Cr^{3+} impurity ions. Most likely, that the present chromium impurity ions are the chromium ions with the lower valence, namely bivalent Cr^{2+} impurity ions. Possible processes for valence change in chromium are the following: 1. $Cr^{2+} \rightarrow Cr^{3+} + e^-$; 2. $Cr^{2+} + V \rightarrow Cr^{3+} + X_s^-$ [26]. Besides, the addition reaction takes place: $Fe^{3+} + Cr^{2+} \rightarrow Fe^{2+} + Cr^{3+}$. This reaction is reversible. Position of the chromium bands observed in our irradiated Pale blue beryl crystals coincides with Cr^{3+} ions band position in emerald [1], only the bands for irradiated crystals are wider, than in emerald. Broadening of spectral bands is connected with decrease of Cr^{3+} local symmetry. Decrease of the local symmetry is associated with formation of a complex center. We suppose that the bands in region from 690 to 588 nm belong to a complex center, which consists of Cr^{3+} ion and a radiation defect (F or F^+ center – an anion vacancy, which captures one or two

electrons). Concentration of F and F⁺ centers increases with neutron fluence increasing. The number of perturbed chromium sites also increases and the band becomes more intense. Appearance of the additional bands due to exchange interaction between F or F⁺-centers and transition metal impurity ions has been previously noted in MgF₂, MgAl₂O₄ and MgO [28-32]. In contrast to paper [24-26] our crystals retain the acquired color. We suppose that presence of Fe²⁺ ions in beryl crystals contributes to the color persistence.

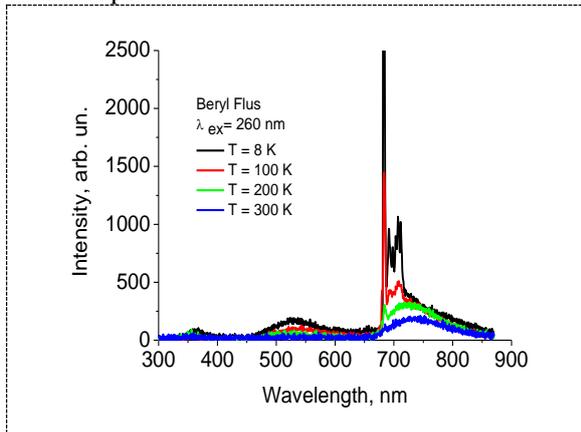


Figure 3. Photoluminescence spectra of Beryl Flux crystal at different temperatures, excitation wavelength 260 nm.

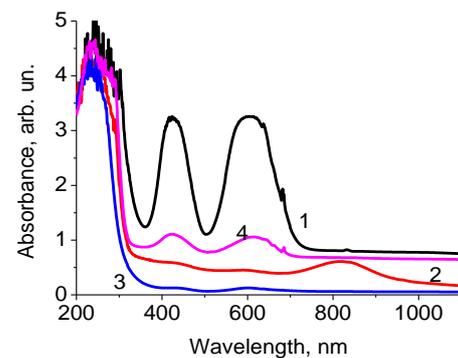


Figure 4. Beryl absorption spectra: 1. synthetic beryl Cr 0.1%, 2. Natural green beryl from Ural-1, 3. synthetic Beryl Flux, 4. synthetic Beryl M.

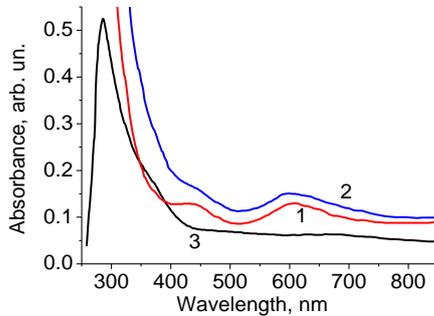


Figure 5. Absorption spectra of Natural green beryl-2: 1. before irradiation, 2. after fast neutron irradiation $\Phi=10^{16}\text{cm}^{-2}$, 3. additional absorption spectrum (2-1).

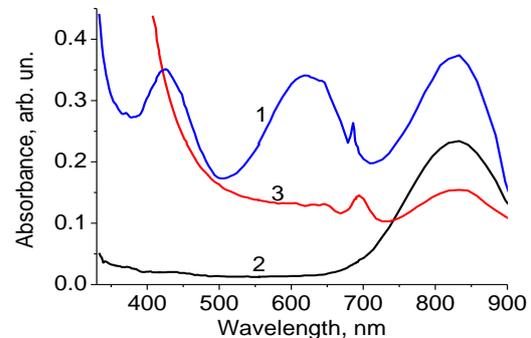


Figure 6. Absorption spectra of: 1. Natural green beryl-3, 2. Pale blue beryl before irradiation, 3. Pale blue beryl after fast neutron irradiation $\Phi=10^{16}\text{cm}^{-2}$.

4. Conclusions

The photoluminescence and optical absorption of natural and synthetic beryl $\text{Be}_3\text{Al}_2\text{Si}_6\text{O}_{18}$ crystals containing chromium and iron ions and defects produced by fast neutron irradiation fluence 10^{16}cm^{-2} ($E > 0.1\text{ MeV}$) has been investigated.

From the PL measurements it follows that all studied beryl samples contain emission bands due to the presence of iron and chromium ions. In the absorption spectra of natural beryl samples, which have no Fe²⁺ band, irradiation by fast neutrons causes appearance only of bands typical for radiation defects (F or F⁺- centers), whereas in absorption spectrum of natural Pale blue beryl crystals, which have Fe²⁺ band, such irradiation leads to rise of the absorption bands in the region 690-580 nm, which belong to

a complex center consisting of Cr³⁺ ions and radiation defects. Presence of Fe²⁺ ions contributes to the persistence of the complex defect.

5. Acknowledgments

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