Optical Properties of Irradiated Topaz Crystals

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Abstract. The results of an investigation of UV-Visible absorption and photoluminescence spectra of colorless topaz before and after neutron irradiation, natural blue topaz from Ukraine, and yellow topaz are presented. We assume that the absorption band ~ 620 nm and broad emission band 300-700 nm in topaz crystals are associated with exchange interaction between a radiation defect (anion vacancies, which capture one or two electrons) and impurity ions Cr$^{3+}$, Fe$^{3+}$, and Mn$^{2+}$.

1. Introduction

Even small amounts 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 topaz crystals. Topaz crystals have been investigated as a possible candidate for dosimetry [1]. Topaz is an aluminium fluorosilicate with a general composition of Al$_2$(SiO$_4$)(F,OH)$_2$. The structure of topaz consists of SiO$_4$ groups linking octahedral chains of Al[O$_4$(F,OH)$_2$] in a zigzag fashion parallel to the crystalline c-axis. Four of six anions surrounding Al$^{3+}$ ion belong to a SiO$_4$ tetrahedron and the remaining two anions are F$^-$ or OH$^-$ group. Topaz crystallizes in the orthorhombic system, space group Pbnm (D$_{2h}^{16}$) [2, 3] with four molecules per unit cell, but the OH/F substitution turns its symmetry into triclinic (P1) [4]. Coloration of topaz crystals is possible through the incorporation of transition metal impurities or by irradiation. Blue topaz now is one of the gem industry’s most commercialized gemstones. The origin of the blue color in topaz is not well understood. Some authors attributed blue color to a broad absorption band generated by the so-called R-centers (two F-vacancies with two trapped electrons [5], whereas others attributed it to an O$^-$ center interacting with two Al ions of the topaz structure. This O$^-$ center is produced by the irradiation in the hydroxyl sites, which substitutes for fluorine in the topaz structure [6-9]. As suggested by Priest V. at al [10] the blue defect in neutron damaged topaz is the doubly occupied dangling silicon bond.

We present a study of optical properties of topaz crystals from India and natural topaz crystals from Ukraine before and after fast neutron irradiation.

2. Materials and Methods

Yellow topaz from India and natural colorless and blue topaz from Ukraine were investigated. The samples thickness was in the range of 1.8 –3.4 mm.

The neutron irradiation was performed at the Latvian 5 MW water-water research reactor. The fluence of fast neutrons with energy > 0.1 MeV was in the range $10^{14} – 5\cdot10^{17}$ cm$^{-2}$. A cadmium filter
was used for absorption of thermal neutrons. The sample temperature did not exceed 40°C during the neutron irradiation.

The photoluminescence (PL) studies were carried out using a conventional setup for spectral measurements. The setup was equipped with a UV-laser DTL-389QT (λ =263 nm), with pulse energy 4.7 mJ at 1kHz, or deuterium lamp LDD-400 as a source of UV light and a grating monochromator MDR-2 in the excitation channel. In the case of PL measurements the luminescence signal was analyzed by Shamrock monochromator SR-303i-B using a grating with 150 lines/mm and 500 nm blaze and detected with a CCD camera DV420A-BU2 in the accumulation mode.

The standard technique for absorption measurements has been based on a “Specord 210” (Analytikjena) double-beam spectrophotometer operating in the spectral region of 190-1100 nm. Optical measurements before and after irradiation were carried out at the temperature 300 K.

3. Results and Discussion

The absorption spectra of topaz single crystals before irradiation (curve 1), after fast neutron irradiation (curve 2), natural blue topaz from Ukraine (curve 3) and yellow topaz (curve 4) are given in Figure 1. Before fast neutron irradiation in absorption spectra of colorless topaz there was observed only one band at 230 nm. After irradiation intensity of the absorption band 230 nm increases and there appear bands with maxima at 305, 430 and 620 nm and crystals obtain blue color. In natural blue topaz there was identified an intensive band at 230 nm and less intensive bands at 430 and 620 nm. In the absorption spectrum of yellow topaz there were also observed bands in the region 230-305 nm, moreover, there was observed a weak band at 500 nm. Two lines around 230 and 305 nm belong to a single defect such as silanone (=Si=O) as it was suggested in [11] basing on similar lines observed in spodumene. The increasing of fast neutrons fluence to $10^{17}$ cm$^{-2}$ leads to an increase of the concentration of such defects. The calculations performed in [12] using AlCrFH$_4$O$_7$Si model molecule with unrestricted CIS method to simulate UV and visible spectra shows that the theoretical spectrum of the model is in a considerably good agreement with experimental one. Excitation spectra of Cr$^{3+}$ investigated by Tarashchan A N at al. [13] in topaz crystal show the same lines. Albuquerque A R P L at al. suggested that band 620 nm is due to a lattice defect [14].

We assume that the band ~ 620 nm includes not only so-called R-centers (two F-vacancies with two trapped electrons) or doubly occupied dangling silicon bands, but also the bands associated with the presence of impurities of Cr$^{3+}$, Fe$^{3+}$ and Mn$^{2+}$ ions. Band 430 nm also belongs to impurity Cr$^{3+}$ion.

The photoluminescence spectra of topaz crystals excited by laser at $\lambda =263$ nm are shown in Fig. 2. In the photoluminescence spectra of nonirradiated topaz crystal there are two bands at 700 and 540 nm (Fig. 2, curve 1). After fast neutron irradiation the band at 700 nm disappears and a broad band 460 nm with shoulder 380 nm is observed (Fig. 2, curve 2). The fluence rise to $5 \times 10^{17}$ cm$^{-2}$ leads to considerable reduction of intensity of a band at 460 nm (Fig. 2, curve 3). The intensive band at 460 nm with shoulder 700 nm is observed in natural blue crystals (Fig. 2, curve 4). The photoluminescence spectra of yellow topaz contain two bands with maxima 740 and 570 nm (Fig. 2, curve 5). Fig. 3. depicts the lines obtained from decomposition of the spectra of nonirradiated and irradiated by fast neutron fluence $\Phi = 10^{17}$ cm$^{-2}$. Photoluminescence bands in topaz crystal before irradiation are connected with Cr$^{3+}$ (band ~ 700 nm), Fe$^{3+}$ (band 740 nm), Mn$^{2+}$ (band ~ 560 nm) and peroxy-radical (band ~465 nm) [15-18]. Photoluminescence spectra of natural blue topaz crystals excited by the laser ($\lambda = 263$ nm) and the excited by lamp ($\lambda =230$ nm and $\lambda =260$ nm) and results of the curve fitting (band shapes are assumed to be Gaussian) are given in Fig. 4. When exposed with UV light, topaz samples showed a very weak luminescence (Fig. 4, curves 2 and 3). Excitation with light 230 nm leads to the appearance of a 400 nm band. The same band is observed in photoluminescence spectra of irradiated topaz after curve fitting. Excitation of natural blue topaz with light of 260 nm produces a band with maxima~ 465 nm, without a shoulder at 400 nm. Photoluminescence characteristics of variously colored topazes are caused by Cr$^{3+}$ entering the octahedral site of the topaz structure. Taking into account that the Cr incorporation in topaz is related to the F/OH distribution [19], Cr$^{3+}$ may be coordinated differently by O$_3$F$_2$, O$_2$FOH or O$_4$(OH)$_2$. Among three Cr$^{3+}$ complexes, CrO$_4$F$_2$,
CrO$_4$FOH, and CrO$_4$(OH)$_2$, the second has certainly a more distorted crystal field than the first and the third.

It is evident that the broad emission line 300-700 nm is connected with complex centers, because it appears after neutron irradiation. The presence of nearby anion vacancies, which capture one or two electrons may modify the environment at the Cr$^{3+}$ impurity site to produce an effective increase in the crystal field. In additional to the shift in energy, the perturbation induced by the anion vacancies, which capture one or two electron ($F^-$ or $F^+$- center) can increase the oscillator strength by introducing...
odd components to the crystal field, or by exchange coupling between the $F^-$ or $F^+$ center and the Cr$^{3+}$ impurity. The enhancement of the oscillator strength by the exchange interaction has been previously observed in MgF$_2$, MgAl$_2$O$_4$ and MgO [20-23]. With the concentration increase of anion vacancies, which capture one or two electrons, the number of perturbed chromium sites also increased, so that the excitation peaks became more intense as a function of neutron dose. Further fast neutron fluence increasing over $5 \times 10^{17}$ cm$^{-2}$ leads to decrease of photoluminescence bands intensities - this may be connected with topaz lattice disorder [24].

4. Conclusion
The UV-Visible absorption spectra and photoluminescence spectra of yellow, natural blue and colorless topaz crystals from Ukraine before and after exposure to a fluence of fast neutrons up to $5 \times 10^{17}$ cm$^{-2}$ (E$>$0.1 MeV) are investigated. We assume that the absorption band ~ 620 nm and broad emission band 300-700 nm in topaz crystals are associated with exchange interaction between a radiation defect (anion vacancies which capture one or two electron) and impurity ions Cr$^{3+}$, Fe$^{3+}$ and Mn$^{2+}$.

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References