

# Optical properties of natural topaz

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**Abstract.** The results of investigation of infrared, Raman and UV-Visible absorption spectra of natural topaz crystals from Ukraine before and after fast neutron irradiation are presented. We assume that the  $\sim 620$  nm band in topaz crystals is associated with the presence of  $\text{Cr}^{3+}$ ,  $\text{Fe}^{2+}$  and  $\text{Mn}^{2+}$  impurities. The broad band with maxima at  $650\text{ cm}^{-1}$  observed in Raman spectra for topaz irradiated by fast neutrons may be connected with lattice disorder. Exchange interaction between radiation defect and impurity ions during neutron irradiation leads to appearance of additional absorption band in UV-VIS spectra and bands broadening in infrared and Raman spectra of investigated crystals.

## 1. Introduction

The study the optical properties of topaz can be used to determine the quality of jewelry topaz, for the successful use of these crystals in thermoluminescence dosimetry [1] as well as for evaluation of physical and chemical conditions of formation of mineral [2]. Topaz is an aluminium fluorosilicate with a fairly constant chemical composition  $\text{Al}_2\text{SiO}_4(\text{OH},\text{F})_2$ . The only major variation found in different samples is related to the  $[\text{OH}]/[\text{F}]$  concentration ratio. The structure of topaz consists of  $\text{SiO}_4$  groups linking octahedral chains of  $\text{Al}[\text{O}_4(\text{F},\text{OH})_2]$  in a zigzag fashion parallel to the crystalline c-axis. Four of six anions surrounding  $\text{Al}^{3+}$  ion belong to  $\text{SiO}_4$  tetrahedron and the remaining two anions are  $\text{F}^-$  or  $\text{OH}^-$  group. Topaz crystallizes in the orthorhombic system, space group  $\text{Pbnm}$  ( $\text{D}_{2h}^{16}$ ) [3, 4] with four molecules per unit cell, but the OH/F substitution turns its symmetry into triclinic (P1) [5]. The lattice parameters are  $a=4.6499\text{ \AA}$ ,  $b=8.7968\text{ \AA}$  and  $c=8.3909\text{ \AA}$  and is normally found as well-developed prismatic crystals with pyramidal terminations.

Usually in nature topaz occurs in the form of colorless crystals. 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.

The paper presents study of infrared, Raman and UV-Visible absorption spectra of natural topaz crystals from Ukraine before and after fast neutron irradiation.

## 2. Materials and Methods

Natural colorless and blue topaz from Ukraine was investigated. The sample 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  $> 0.1\text{ MeV}$  was in the range  $10^{14} - 5 \cdot 10^{17}\text{ cm}^{-2}$ . A cadmium filter



was used for absorption of thermal neutrons. The sample temperature did not exceed 40°C during the neutron irradiation.

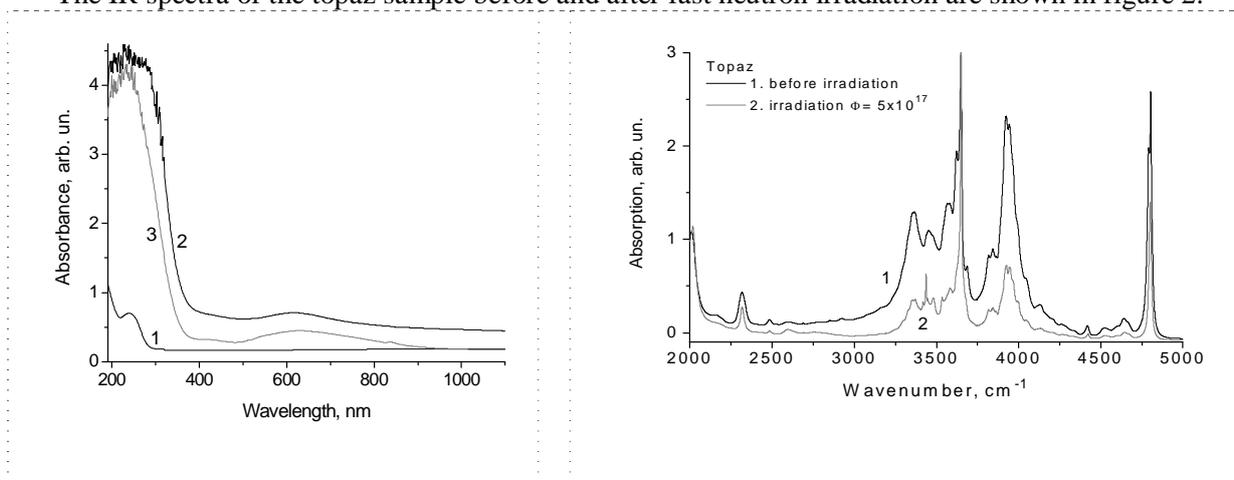
Infrared spectra were measured at room temperature using VERTEX 80v vacuum FT-IR spectrometer with the actively aligned UltraScan™ interferometer, which provides peak spectral resolution. Raman spectra were measured by Raman Spectrometer Advantage 785 (USA) with laser 785 nm.

The standard technique to measure absorption spectra 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) and natural blue topaz from Volodarsk Volynskii, Ukraine (curve 3) 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 the absorption band 230 nm intensity 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. Two lines around 230 and 305 nm belong to a single defect such as silanone (=Si=O) as it was suggested in [6] basing on similar lines observed in spodumene. Blue color is connected with a broad absorption band in the red part of the spectrum generated by the so-called R-centers (two F-vacancies with two trapped electrons) [7]. It was previously concluded that the optical absorption band centered at 620 nm is closely correlated with 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 [8, 9]. As suggested Priest V. et al [10] the blue defects in neutron damaged topaz is the doubly occupied dangling silicon bond. The calculations performed in [11] using  $AlCrFH_7O_{11}Si$  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 et al. [12] in topaz crystal show the same lines. We assume that the band ~ 620 nm includes not only the above mentioned bands, but also the bands associated with the presence of impurities of  $Cr^{3+}$ ,  $Fe^{2+}$  and  $Mn^{2+}$  ions. Band 430 nm also belongs to impurity  $Cr^{3+}$  ion.

The IR spectra of the topaz sample before and after fast neutron irradiation are shown in figure 2.



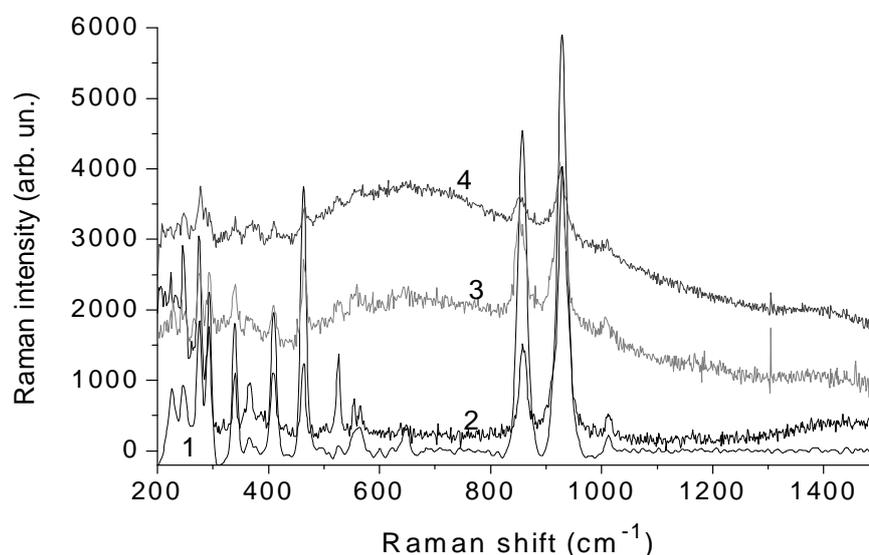
**Figure 1.** Topaz absorption spectra before (1) and after neutron irradiation (2), (3) natural blue topaz from Volodarsk Volynskii, Ukraine.

**Figure 2.** Infrared spectra of topaz crystals:

1. before fast neutron irradiation, 2. after irradiation  $\Phi = 5 \cdot 10^{17} \text{ cm}^{-2}$ .

The hydroxyl ions are normally configured into the mineral assembly as crystallization water or as hydroxyl ion replacing other ions of the structure. Depending on its origin topaz always contains hydroxyl groups which substitute for fluorine atoms. The ratio OH/(OH+F) varies from almost zero up to thirty percent. When the OH content becomes sufficient, the structure is distorted to triclinic or monoclinic symmetry. OH- stretching mode is observed on wave number around  $3650\text{cm}^{-1}$ , with a strong asymmetry around  $3622\text{cm}^{-1}$ . The observed OH stretching vibrations are in good agreement with the position of approximately  $3650\text{cm}^{-1}$  for band observed in [13, 14] and calculated by Churakov [15]. The band at  $3650\text{cm}^{-1}$  was decomposed in two components at  $3639$  and  $3650\text{cm}^{-1}$ . These two peaks were assigned to two vibrations (stretching modes) of the OH molecules substituting for F [16]. Additionally, a broader and weaker band was observed around  $3450\text{cm}^{-1}$  assigned earlier due to anomalous OH group [17]. Before irradiation of colourless topaz in infrared spectra there were observed two bands around  $4809$  and  $4787\text{cm}^{-1}$ , which are the combination of main (OH) stretching and Al-OH bending modes ( $1163\text{cm}^{-1}$ ) as suggested in [18]. Fast neutron irradiation reduces this band intensity and band became symmetrical with maximum  $4802\text{cm}^{-1}$ . Bands around  $3950\text{cm}^{-1}$  were observed. After fast neutron irradiation bands intensities decrease, and only the  $3650\text{cm}^{-1}$  band intensity increases. Neutron irradiation produces the electron and hole defects in topaz crystals. They probably interact with impurities and hydroxyl ions and reduce the local symmetry

Raman spectra of natural blue topaz, colourless topaz and irradiated by fast neutron at fluence  $\Phi = 10^{17}\text{cm}^{-2}$  and  $5 \times 10^{17}\text{cm}^{-2}$  are shown in figure 3. Spectra of natural blue and colourless topaz analysed in this work are comparable to those found in the literature. The bands observed around  $276\text{-}293\text{cm}^{-1}$ ,  $561\text{cm}^{-1}$ ,  $858\text{cm}^{-1}$ ,  $929\text{cm}^{-1}$ ,  $1006\text{cm}^{-1}$  are assigned to the various Si-O vibration modes in  $\text{SiO}_4$  group based on the work of Griffith [19], Beny and Piriou [16] and Souza [20], the bands between  $235$  and  $380\text{cm}^{-1}$  are considered to be caused by the symmetric Si-O ring deformation, and the bands between  $300$  and  $400\text{cm}^{-1}$  are satellite bands [13]. The series of sharp bands in the  $330 - 500\text{cm}^{-1}$  range are assigned with stretching and bending modes of  $[\text{AlO}_6]$  octahedral coupled with the bending modes of  $[\text{SiO}_4]$  tetrahedra. The band observed at  $325\text{cm}^{-1}$  is assigned to Al-F stretching modes [13].



**Figure 3.** Raman spectra of topaz crystals: 1. natural blue, 2. before and 3. after fast neutron irradiation  $\Phi = 10^{17}\text{cm}^{-2}$ , 4.  $\Phi = 5 \cdot 10^{17}\text{cm}^{-2}$ .

The Raman spectrum of colourless topaz (figure 3) before irradiation is the same as that of the natural blue topaz. Intensities of some bands for these two crystals slightly differ. After fast neutron irradiation the broad band with maxima at  $650\text{ cm}^{-1}$  are observed. The narrow lines intensities decrease (figure 3, curve 3 and 4) with fast neutron fluence increasing. The narrow lines intensities decrease and broad band appearance may be connected with topaz lattice disorder.

#### 4. Conclusion

The infrared, Raman and UV-Visible absorption spectra of natural topaz crystals from Ukraine before and after exposure to a fluence of fast neutrons up to  $5 \cdot 10^{17}\text{ cm}^{-2}$  ( $E > 0.1\text{ MeV}$ ) are investigated. We assume that the band  $\sim 620\text{ nm}$  in topaz crystals is associated with the presence of impurities of  $\text{Cr}^{3+}$ ,  $\text{Fe}^{2+}$  and  $\text{Mn}^{2+}$  ions. The broad band with maxima at  $650\text{ cm}^{-1}$  observed in Raman spectra for irradiated by fast neutron topaz may be connected with lattice disorder. Exchange interaction between radiation defect and impurity ions during neutron irradiation leads to appearance of additional absorption band in UV-VIS spectra and bands broadening in infrared and Raman spectra of investigated crystals.

#### 5. Acknowledgments

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#### References

- [1] Magalhaes C M S, Macedo Z S, Valerio M E G, Hernandez A C and Souza D N 2004 *Nuclear Instruments and Methods in Physics Research B* **218** 277
- [2] Ivanova O A and Korovkin M V 2001 *Izvestija Tomskogo politehnicheskogo universiteta* **304** 85 (in Russian)
- [3] Ribbe P H and Gibbs G V, 1971 *Am. Mineral.* **56** 24
- [4] Northrup P A, Leinenweber R and Parise J B 1994 *Am. Mineral.* **79** 401
- [5] Pinheiro M V B, Fantini C, Krambrock K, Persiano A I C, Dantas M S S and Pimenta M A 2002 *Phys. Rew. B* **65**, 104301
- [6] Bonventi W Jr, Isotani S and Albuquerque A R P L 2012 *Advances in Condensed Matter Physics Article ID 873804*. doi:10.1155/2012
- [7] Platonov A N, Taran M N and Balyatskii V S 1984 *Nature of color gems* (Moscow: Nedra) (in Russian).
- [8] Da Silva D N, Guedes K J, Pinheiro M V B, Spaeth J-M and Krambrock K 2005 *Phys. Chem. Minerals* **32** 436
- [9] Leal A S, Krambrock K, Ribeiro L G M, Menezes M A B C, Vermaercke P and Sneyers L 2007 *Nuclear Instruments and Methods in Physics Research A* **58** 423
- [10] Priest V, Cowan D L, Reichel D G and Ross F K 1990 *J. Applied Physics* **68** 3030
- [11] Goto H, Niwa A, Greenhidge D C, Kato N, Ida T, Mizuno M, Endo K and Tada T 2005 *J. of Surface Analysis* **12** 249
- [12] Tarashchan A N, Taran M N, Rager H and Iwanuch W 2006 *Phys. Chem. Minerals* **32** 679
- [13] Kloprogge J T and Frost R L 2000 *Spectrochim. Acta A* **56** 501
- [14] Wunder B, Rubie D C, Ross C R, Medenbach O, Seifert F and Schreyer W 1993 *Amer. Mineral.* **78** 285
- [15] Churakov S V and Wunder B 2004 *Phys. Chem. Minerals* **34** 131
- [16] Beny J M and Piriou B 1987 *Phys. Chem. Minerals* **15** 148
- [17] Aines R D and Rossman G R 1986 *Amer. Mineral.* **71** 1186
- [18] Prasad P S R and Gowd T N 2003 *J Geological Society of India* **61** 202
- [19] Griffith W P 1969 *J Chem. Soc. A* 1372
- [20] Souza D N, Lima J F, Valerio M E G, Fantini C, Pimenta M A, Moreira R L and Caldas L V E 2002 *Nuclear Instruments and Methods in Physics Research B* **191** 230