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Luminescence of dense, octahedral structured crystalline silicon dioxide (stishovite)

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ABSTRACT

It is obtained that, as grown, non-irradiated stishovite single crystals possess a luminescence center. Three excimer pulsed lasers (KrF, 248 nm; ArF, 193 nm; F₂, 157 nm) were used for photoluminescence (PL) excitation. Two PL bands were observed. One, in UV range with the maximum at 4.7 ± 0.1 eV with FWHM equal to 0.95 ± 0.1 eV, mainly is seen under ArF laser. Another, in blue range with the maximum at 3 ± 0.2 eV with FWHM equal to 0.8 ± 0.2 eV, is seen under all three lasers. The UV band main fast component of decay is with time constant $\tau = 1.2 \pm 0.1$ ns for the range of temperatures 16–150 K. The blue band decay possesses fast and slow components. The fast component of the blue band decay is about 1.2 ns. The slow component of the blue band well corresponds to exponent with time constant equal to 17 ± 1 μ s within the temperature range 16–200 K. deviations from exponential decay were observed as well and explained by influence of nearest interstitial OH groups on the luminescence center. The UV band was not detected for F₂ laser excitation. For the case of KrF laser only a structure less tail up to 4.6 eV was detected. Both the UV and the blue bands were also found in recombination process with two components having characteristic time about 1 and 60 μ s. For blue band recombination luminescence decay is lasting to ms range of time with power law decay $\sim t^{-1}$.

For the case of X-ray excitation the luminescence intensity exhibits strong drop down above 100 K. such an effect does not take place in the case of photoexcitation with lasers. The activation energies for both cases are different as well. Average value of that is 0.03 ± 0.01 eV for the case of X-ray luminescence and it is 0.15 ± 0.05 eV for the case of PL. So, the processes of thermal quenching are different for these kinds of excitation and, probably, are related to interaction of the luminescence center with OH groups.

Stishovite crystal irradiated with pulses of electron beam (270 kV, 200 A, 10 ns) demonstrates a decrease of luminescence intensity excited with X-ray. So, irradiation with electron beam shows on destruction of luminescent defects.

The nature of luminescence excited in the transparency range of stishovite is ascribed to a defect existing in the crystal after growth. Similarity of the stishovite luminescence with that of oxygen deficient silica glass and induced by radiation luminescence of α -quartz crystal presumes similar nature of centers in those materials.

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1. Introduction

Silicon dioxide could exist in many polymorph modifications. Polymorph modifications based on ability of silicon to sp^3 hybridization belong to a family of tetrahedron structured materials and that family could be accounted as mostly studied from fundamental science and application point of view. Dense (4.28 g cm^{-3}), octahedron structured polymorph modification named stishovite is not

well studied, however theoretical and experimental approaches of study are started now and the first results are obtained [1–5].

Main element of structure of dense silicon dioxide—stishovite is based on another manner of silicon hybridization— d^2sp^3 , providing octahedral surrounding of silicon with oxygen ions. Our interest is in the study of change of electronic states and point defects in a way from tetrahedron structured modification to octahedron structured modification of silicon dioxide. We account that our knowledge of tetrahedron structured modifications of silicon dioxide is more eminent than that for octahedron structured modifications then the last should be studied more. Electron states and point defects examination with optical methods are widely used and we targeted those methods for octahedral silicon dioxide.

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Actually, it is little known about defects in stishovite. The role of hydrogen in the form of OH group was studied [6,7]. In Ref. [6] it was found that in Raman spectra there are no lines corresponding to OH bond. In Ref. [7] it was determined that IR spectra containing optical absorption bands corresponding to OH. The influence of iron and aluminum impurity on OH IR absorption band intensity was studied [7]. Samples, with and without iron, possess similar intensity of OH absorption, whereas aluminum impurity stimulate intensity of OH IR absorption. Therefore it was concluded that OH impurity could be incorporated into defect structure mainly, host or impurity.

The position of intrinsic absorption threshold was determined for stishovite single crystal and it is situated at 8.75 eV, [4]—being higher than that for main tetrahedron structured silicon dioxide crystal— α -quartz, for which it is about 8.5 eV at room temperature. It is discovered that stishovite single-crystal possesses luminescence with sufficiently high yield both under X-ray or cathode and photo excitations [1,3–5], so luminescence methods could be informative about properties of electronic states and point defect in stishovite crystal.

Luminescence of stishovite single crystal appears both in recombination and intra center processes [1,3–5] and ionizing and photo irradiation. Also for the case of poly-crystals the photoluminescence excitation spectrum was measured [2].

Previous research of stishovite luminescence was not able to answer definitely a question [8] if the luminescence center exists in as received materials or it was created with ionizing irradiation. For resolving that, now we have investigated as received virgin single crystals. Also, we try compensating the lack of data for liquid helium temperature range for photoluminescence spectral-kinetics behavior.

Antecedently, it was noticed that the luminescence of stishovite is very similar to luminescence of oxygen deficient silica glass and neutron, gamma or dense electron beam irradiated α -quartz crystal [9–13]. Oxygen deficient luminescence of silica glass is connected to the so called oxygen deficient center of luminescence (ODC) and now in the literature it is distinguished as several types of ODC. The ODC with relatively clear geometric and energetic model is so called ODC(II) or a twofold coordinated silicon existing in silica glass in small concentration with respect to total level of oxygen deficiency. For that center it is found an absorption band centered at 5 eV, and two luminescence bands a blue one at 2.7 eV and an UV one at 4.4 eV can be excited [14]. The first band luminescence decays exponentially with time constant $\tau=10.3$ ms, which is a characteristic for triplet-singlet transitions. The second band decays with $\tau=4.5$ ns and corresponds to singlet-singlet transitions in ODCs [14]. However oxygen deficient defects of silica glass in much higher concentration are related to so called modified ODC by a nearest defect, or in others words, ODC making a complex with nearest defects [15–18]. The structure of these modified ODC is not yet defined. The parameters of such ODC luminescence are different from those of the lone twofold coordinated silicon center [14], however PL spectra are similar with ODC(II). Now, we will continue comparison of stishovite luminescence with that of ODC in silica and irradiated α -quartz.

2. Experimental procedure

The stishovite single crystals were grown under hydrothermal conditions by methods published in Refs. [17–19,20]. The samples of investigation were small optically transparent single crystals with the dimensions about $0.2\text{--}0.4 \times 0.6 \times 0.9$ mm³. The samples were kept on a copper holder covered with an indium layer possessing a hole, where the samples were pressed into

avoiding slits let light through. The excitation was made from one side of the holder and detection from the other, so excluded the possible luminescence of contamination on the surface of the holder.

The optical absorption was measured with Hamamatsu mini spectrometer and optical fiber using deuterium discharge lamp as light source. Initially, the spectrum of light source was measured through an empty hole approximately of samples dimensions. Then the spectrum of light passed through the sample was measured. The optical fiber was put directly or on the hole or on the sample holder with the sample. The absorption spectra in VUV region were measured on equipment with the 0.5 m Seya-Namioka vacuum monochromator. Others details could be found in Ref. [3]. The spectra of transmittance and absorbance were then calculated in relative units.

The KrF, ArF and F₂ lasers (model PSX-100, made by Neweks, Estonia) as well as X-ray tube were luminescence excitation sources. The F₂ (157 nm) has a pulse energy of about 0.5 mJ with a duration of 5 ns. The KrF (248 nm) and ArF lasers (193 nm) were of 7 times higher power. The light of the F₂ laser was passed through a copper tube with the flow of nitrogen. The light of the KrF, ArF laser was put on the sample through atmospheric air. The excitation laser was situated on 1 m distance from the sample. The beam of the laser is 2 mm \times 2 mm. The crystalline silicon dioxide α -quartz with low level of luminescence was used as window to pass through the light of the excitation lasers. The photoluminescence intensity of studied samples was linearly depending on excitation intensity; therefore the excitation regime was single photon. Monitoring of excitation intensity was realized with LiF crystal plates of different thicknesses, whose attenuation degree was determined with use of a power-meter.

The X-ray tube was with W anticathode working in regime 50 kV, 20 mA. Two cryostats were used. A cryostat maintains temperature in the range 60–400 K. the value 60 K was achieved by pumping of liquid nitrogen from cryostat. Some measurements were realized with the use of helium refrigerator. The temperature range in this case was 16–300 K. Luminescence detection was realized through by means of a grating monochromator MCD-1 with a photomultiplier tube H6780-04 with 50 ohm resistive load. The optical filters were employed for cutting laser light in the line for luminescence detection. An oscilloscope (Textronic TDS 2022B) was exploited for decay curve registration. Each curve was averaged for 128 pulses. The time resolved spectra are measured by registration of the decay curve for each point of the PL spectrum in two time ranges—one in ns range another in μ s range. The measured curves are presented in figures as received therefore they reflect the level of errors. The discharge of excimer laser provides strong stray current in the measurement circuit, which distorts signal for short time range.

The X-ray excited spectra were measured in the photon counting regime with use of PM FEU-106. The PL decay kinetics of long duration and low intensity (unable to be measured in current regime) was recorded with the use of photon pulses time analyzer, made in LU ISSP. The spectra in IR range were measured with FTIR spectrometer Bruker Equinox 55.

3. Results

The optical absorption of studied sample of stishovite single crystal is presented in Fig. 1. Other three measured samples possess similar spectra within experimental errors. Qualitatively that spectra well corresponds to previously measure smaller sample [3], showing the intrinsic absorption threshold at 8.75 eV.

Besides, we had measured IR absorption of stishovite, Fig. 2. The spectra of different samples are in mutual agreement within

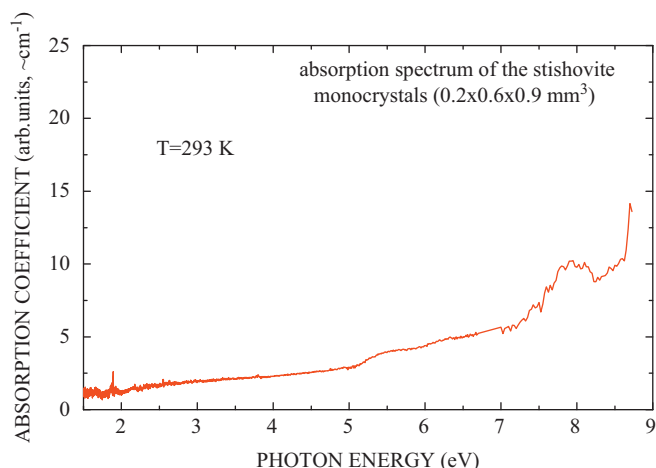


Fig. 1. Optical absorption spectrum of studied stishovite single crystal. The dimensions $0.2 \times 0.6 \times 0.9 \text{ mm}^3$, being too small for correct determination of absolute value of the absorption coefficient. Present data could be accounted as “arbitrary units” allowing estimating absorption coefficient value.

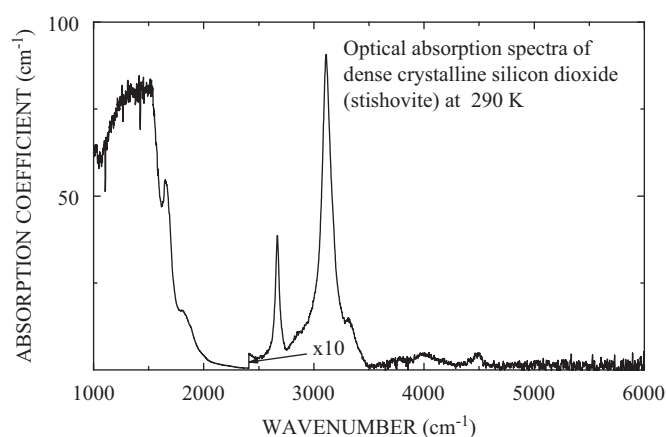


Fig. 2. IR optical absorption spectrum of the stishovite single crystal at 290 K. The bands at 2668 cm^{-1} with FWHM 50 cm^{-1} and $\alpha \sim 3.8 \text{ cm}^{-1}$; 3111 cm^{-1} with FWHM 104 cm^{-1} and $\alpha \sim 9.1 \text{ cm}^{-1}$ are ascribed to presence of the OH-ions in concentration about 20 wt ppm (after [7]). Present data could be accounted as “arbitrary units” allowing estimating absorption coefficient value due to the same reasons as in Fig. 1.

experimental errors. The intrinsic absorption is started below 2000 cm^{-1} and in the transparency range we observe the bands at 2668 cm^{-1} with FWHM 50 cm^{-1} and $\alpha \sim 3.8 \text{ cm}^{-1}$; 3111 cm^{-1} with FWHM 104 cm^{-1} and $\alpha \sim 9.1 \text{ cm}^{-1}$; as well as small bands at 3759 ; 4001 and 4490 cm^{-1} . Comparison with literature data [7] allows us to interpret first two bands connected with the presence of hydroxyl (OH), therefore less intensive bands possibly are due to phonon side bands. The concentration of hydroxyl group could be estimated on the base of data [7] on the level of 20 wt ppm.

Luminescence spectra of one of the studied samples of stishovite are presented in Fig. 3 and those spectra are very similar for different samples. Generally, we observe two broad bands. One is in the blue part of spectra at $3 \pm 0.2 \text{ eV}$ with FWHM equal to $0.8 \pm 0.2 \text{ eV}$. It is observed in all kinds of used excitation—248; 193; 157 nm excimer lasers and as well as under X-ray. Its decay kinetics contain a slow component with time constant about $17 \mu\text{s}$ and a fast component with time constant less than 1.2 ns Fig. 4, insertion. Another band is in the UV part of the spectra with maximum at $4.7 \pm 0.1 \text{ eV}$ with FWHM equal to $0.95 \pm 0.1 \text{ eV}$ Fig. 3. For this band the main decay component is fast with time

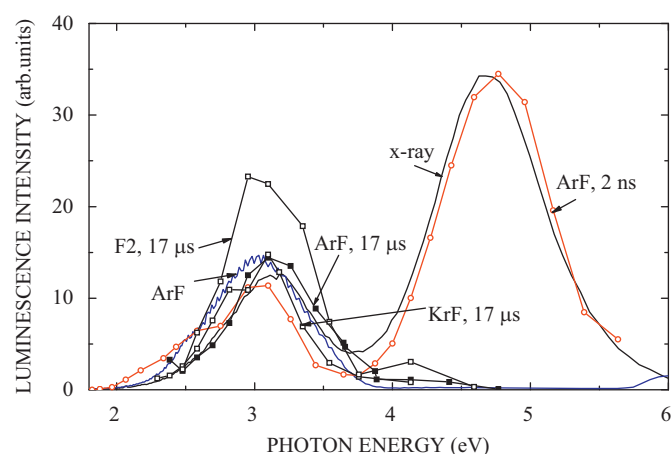


Fig. 3. Photoluminescence (measured on virgin sample first) and X-ray excited luminescence (measured after photoluminescence experiment) spectra of stishovite single crystal sample. X-ray, ArF (193 nm), KrF (248 nm) and F_2 (157 nm) excimer lasers excited, 80 K. Line—continuous regime, points—time resolved.

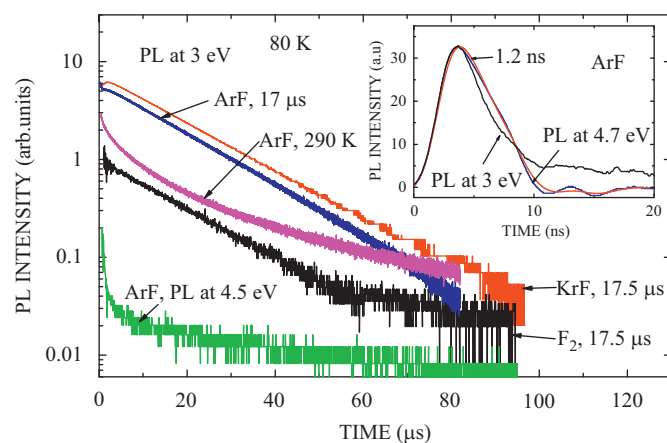


Fig. 4. PL decay kinetics curves of stishovite single crystal excited with excimer lasers and measured in current regime of PM. Slow decay time constant of the blue luminescence is about $17 \mu\text{s}$ and for UV band one component is about $1 \mu\text{s}$ and another is about $60 \mu\text{s}$. Fast components are shown in insertion. Time constant is about 1.2 ns for UV band and for blue band is shorter than 1.2 ns . Estimation of fast component was made by comparing of measured kinetics curve with an exponential decay curve of 1.2 ns time constant convoluted with laser pulse shape.

constant about 1.2 ns Fig. 4, insertion, however a slow component in the time of μs is detected as well Fig. 4. for slow decay there are at least two components. One is about few μs and another about $60 \mu\text{s}$. It was not observed under 157 nm laser. Under 248 nm laser a structure less tail of the band in UV could be detected. This UV band is well observed under 193 nm laser and X-ray irradiation. Cooling from 290 to 80 and to 16 K does not affect significantly the width of the bands. So the width of the bands is determined by other causes than homogeneous broadening.

The main part of decay of the blue PL is exponential with $\tau = 17 \pm 1 \mu\text{s}$ within wide range of temperature 16–200 K Fig. 4, however there are some peculiarities. First, at 290 K under ArF laser we observe strong non-exponential decay, which becomes exponential below 200 K. non-exponential decay could be explained by recombination luminescence additional to intra center excited luminescence. Indeed, measurements with photon counting methods reveal decay in longer time range, being strongly non-exponential and obeying to power law decay, Fig. 5.

Beside main exponential decay of the blue PL with $\tau \sim 17 \mu\text{s}$ and power law low intensity decay of long duration we observe

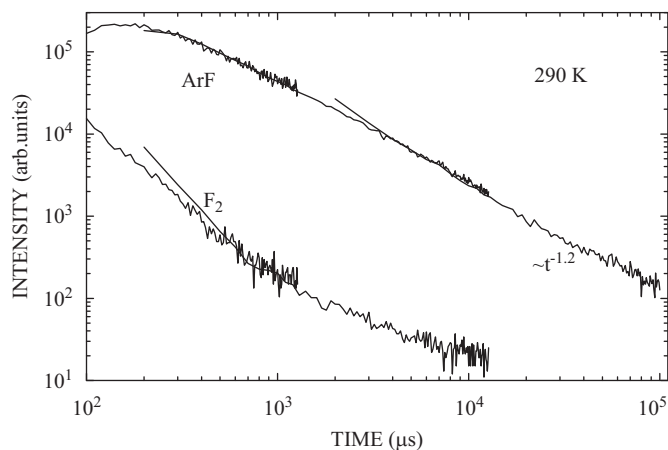


Fig. 5. Blue PL decay kinetics of stishovite single crystal excited by ArF and F_2 lasers and measured with photon counting regime. Curves are measured in different time scale of an analyzer and sewed. Initial growth in kinetics is related to limitation of the photon counting method for high intensity of luminescence in shorter time scale.

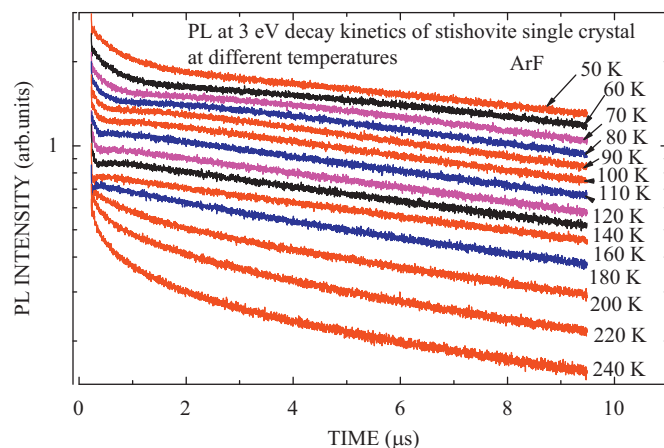


Fig. 7. PL decay kinetics curves of stishovite single crystal excited with ArF excimer laser at different temperatures. The curves are multiplied by an arbitrary factor that to separate them.

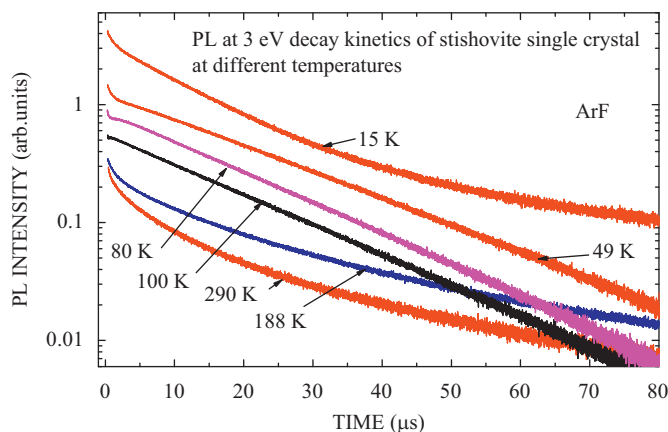


Fig. 6. PL decay kinetics curves of stishovite single crystal excited with ArF excimer laser at different temperatures. The curves are multiplied by an arbitrary factor that to separate them.

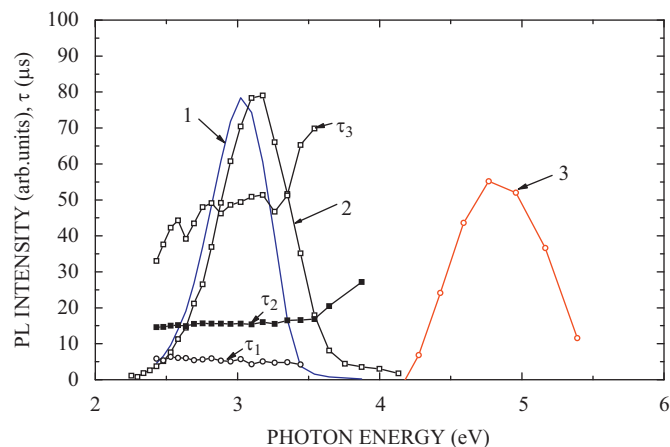


Fig. 8. Time resolved PL and time constants spectra of the stishovite single crystal excited by ArF laser at 16 K. 1—PL intensities are obtained with integration of decay curves in time range 1–100 μ s. 2—intensities are obtained with integration in time range 0–1 μ s. 3—integration in time range 0–30 ns. τ_1 , τ_2 , τ_3 are spectral dependences of decay time constants for different components of decay for blue luminescence.

peculiarity in decay, manifesting themselves as intensity growth at about 5 μ s, Figs. 4, 6 and 7. That is observed for all excimer lasers excitation and all studied samples. It could not be connected with PM overload, because this growth is also obtained with diminishing of light intensity falling into PM by diminishing of the slits of the monochromator. The position of this growth is changed with temperature, Figs. 5 and 6. At 290 K in this part of time we observe a faster decay, Figs. 4–6. The energy activation of this thermally activated process was obtained to be 0.031 eV and corresponding frequency factor is about $5 \times 10^6 \text{ s}^{-1}$. The expression used for that is Mott's expression [21] for time constant:

$$\tau = \tau_0(1 + f \times \tau_0 \exp(-E/kT))^{-1} \quad (1)$$

where τ_0 is the time constant non affected by temperature, f —frequency factor, E is the activation energy, T —temperature, k —Boltzmann constant.

Several components of decay appear at 16 K for blue luminescence, Figs. 6–8 without significant changes within luminescence band. The blue PL band is shifted to higher energy for fast (ns) component Fig. 8; however for wide time ranges from 1 to 100 μ s the position is the same for all component of decay. The UV band corresponding to fast component is delivered Fig. 8, curve 3.

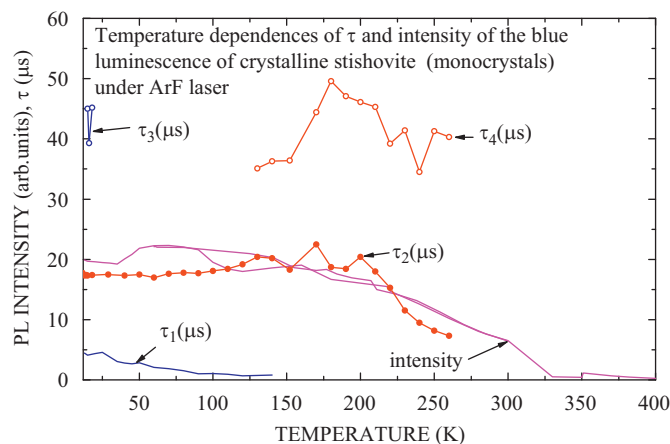


Fig. 9. Temperature dependences of time resolved blue PL intensity, obtained by integration of the decay curves, and time constants of different components of decay for stishovite single crystal excited with ArF laser.

The temperature dependences for the blue PL parameters, determined from decay curves shown in Figs. 4, 6 and 7 are presented in Fig. 9. We observe correspondence between PL

intensity and decay time constants temperature dependences. The appearance of longer decay component with $\tau \sim 50 \mu\text{s}$ (τ_4) above 200 K we connect with appearance of long duration decay of recombination luminescence, Fig. 5. There is a similarity of dependences $\tau_2(T)$ and $I(T)$ at least for range 16–250 K. We observe another peculiarity in the time range below 20 K. The intensity there does not present such big changes with temperature as time constants (τ_1 , τ_3) behavior does in low temperature cases. We have at least three components, Figs. 4–9. One is with increasing τ_1 below 100 K and reaching value of $6 \mu\text{s}$ at 16 K. The parameters of thermal activation for this part are $E_a = 0.01 \text{ eV}$ and $f = 5 \times 10^5 \text{ s}^{-1}$. Another is the main component of decay of $17 \mu\text{s}$ (τ_2 , Fig. 9) in the same temperature range. Below 20 K a component of long duration (τ_3) appears, being $50 \mu\text{s}$ at 16 K.

The X-ray excited spectra are presented in Fig. 10. It is need to underline that the X-ray excitation in this investigation was performed only after PL measurements. The same two bands in the blue and UV parts of spectra are observed in the X-ray excited spectrum. Nothing was changed in PL before and after X-ray excitation, showing little influence of X-ray irradiation on luminescence center. Irradiation with an electron beam was performed, Fig. 10. It was obtained that irradiation with electron beam strongly diminishes X-ray excited luminescence. So, such irradiation does not provide luminescence center in the sample under investigation. Even such irradiation, seems, destroys them.

The temperature dependences of intensity for X-ray excited both bands, measured with photon counting method are presented in Fig. 11. These data are compared with those of time resolved intensity of the blue and UV PL as well as with time constants temperature dependences of both bands for stishovite single crystal excited with ArF laser. A strong effect was observed: significant fall down in intensity of X-ray excited luminescence at 100 K does not corresponds to changes in PL parameters thermal dependences. The parameters of thermal dependences were determined correspondingly to Mott's law analogous to Eq. (1) already presented above for time constant:

$$I(T) = I_0(1 + f\tau_0 \exp(-E_a/kT))^{-1} \quad (2)$$

Where I is intensity and I_0 is intensity of non-quenched transitions. The activation energies for both cases are different as well. Average value of $E_a = 0.03 \pm 0.01 \text{ eV}$ frequency factors are $f(\text{UV}) = 10^{11} \text{ s}^{-1}$, $f(\text{blue}) = 10^7 \text{ s}^{-1}$, for the case of X-ray and $E_a = 0.15 \pm 0.05 \text{ eV}$ frequency factors are $f(\text{UV}) = 10^{12} \text{ s}^{-1}$,

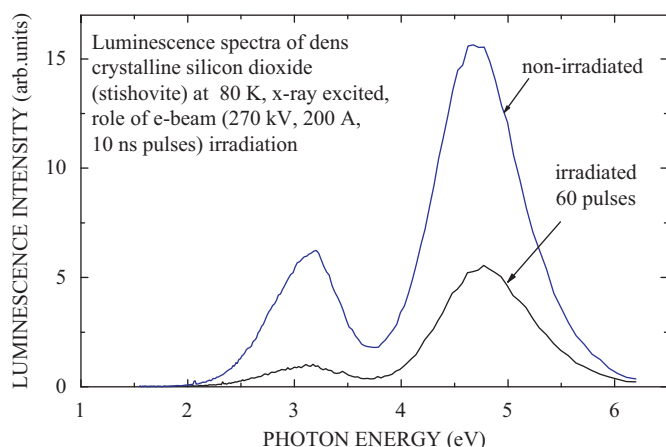


Fig. 10. X-ray excited spectra of the stishovite single crystal measured before and after irradiation with electron beam cannon (270 kV, 200 A, 10 ns duration of pulse) pulses, 0 K.

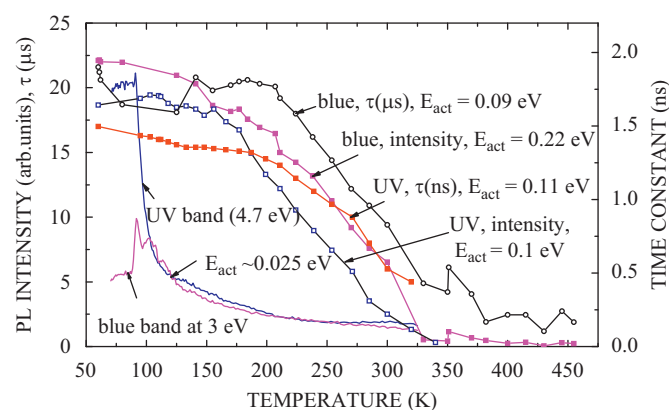


Fig. 11. Temperature dependences of X-ray excited blue and UV bands intensities, time resolved PL intensities (obtained by integrating the decay curves) and decay time constants of principle part of decay excited with ArF laser. The energies of thermal quenching calculated after (1,2) are presented as well. Temperature dependences of X-ray excited (lines) and ArF laser (points) the UV and the blue luminescence of crystalline stishovite (monocrystals).

$f(\text{blue}) = 10^9 \text{ s}^{-1}$, for the case of PL. So the processes of thermal quenching are different for these kinds of excitation.

4. Discussions

We have observed luminescence in as grown single crystal of dense silicon dioxide polymorph modification—stishovite. The luminescence centers exist in non-irradiated samples. Previously, we had some doubt about that [8]. The luminescence possesses two main bands, as it was obtained previously for irradiated sample [1,3–5,8]. One blue band possesses time constant about $17 \mu\text{s}$ in the range 16–200 K and, because of long duration, it is due to forbidden transitions for intra center process. The UV band is fast with τ about 1.2 ns and it is due to allowed transitions. Both bands also could be excited in recombination process. Both bands perform thermal quenching in the same temperature range Fig. 11 and therefore could be ascribed to the same center.

The samples possess OH groups, detected with IR absorption spectra measurement, Fig. 2. As mentioned, OH groups in stishovite could be connected mainly with defects [6,7] in general and, in our particular case, to defect providing luminescence center. Interaction of the PL center with OH groups, creating a complex PL center–OH group could explain peculiarities in decay kinetics. Laser irradiation provokes photolytic reaction for this complex, changing bonding and distances. Normally, an OH group, interacting with a luminescence center provides luminescence quenching effect in the case of many centers (see e.g. Ref. [22]). Remove of OH group by absorption of photon activates the luminescence center [22]. Different distances of luminescence center and separated OH group could change population on the excited state, modulating decay kinetics. Indeed, on the main decay kinetics curve for blue luminescence besides well defined exponential decay with mentioned $17 \mu\text{s}$, we have that curve bending with component of growth in time of range of μs units as well as a fast component of the blue emission in ns time range. Nearest OH group could affect living time on the excited state.

The effect of strong fall down at 100 K in X-ray and lack of such decrease in intensity of PL at that temperature could be explained by differences of OH interaction of center making radiation transitions in intra center process and recombination process. X-ray luminescence appears in recombination process mainly. Probably, the OH groups are modulating the charge trapping.

Perhaps, the OH group could be separated from the center above 100 K, which is a threshold of the OH group motion in studied material. Above 100 K OH can easily come back to the center and quench the luminescence.

As previously [1,3–5,8], we connect luminescence of as received single crystal of stishovite with similar luminescence (also two bands blue and UV) in as received oxygen deficient silica glasses [14–18] and analogous luminescence center in α -quartz crystal induced [10–13] with damaging radiation (γ , neutron and dense electron beam). In these cases there are two luminescence bands corresponding to singlet–singlet transitions with fast decaying UV band and triplet–singlet transitions with slow decaying blue band. However there is no one-to-one correspondence between luminescence centers in silica glass, irradiated α -quartz and stishovite. ODC luminescence of silica glasses, with which we compare luminescence of stishovite, is well studied for dry silica (see for example Refs. [14–17]), therefore one-to-one correspondence between glass and stishovite is not possible because of OH groups influence in the last. From the other hand, if we use for comparison wet silica, there is significant difference in OH groups' incorporation into silica glass and crystals. In the crystals OH group are in form of interstitial, in silica glass main OH position is to be incorporated in the glass network as Si–O–H. Therefore there is no possibility for one-to-one comparison of studied luminescence centers in OH containing stishovite and wet silica glass. Influence of OH groups in irradiated α -quartz crystal is not yet studied, however interstitial incorporation of OH in the lattice of α -quartz crystal presumed being similar to stishovite.

The UV band decay in stishovite is faster than that of UV band in silica glass. In stishovite the decay of the blue band (17 μ s) is faster than that for blue band in silica glass (10 ms). Evidently, in stishovite mono crystal there is no center like the twofold coordinated silicon center in oxygen deficient silica glass. The luminescence center in stishovite more resembles modified ODC of silica glass [15–18]. The luminescence center in stishovite as a core could have a structure like twofold coordinated silicon but strongly modified by some defects, which certainly are different from silica glass defects modifying ODC. On the other hand similar to silica glass ODC luminescence never found in tetrahedron structured α -quartz. Only damaging irradiation produces some similar center [9–13]. So, the ODC luminescence could not be determined with tetrahedron structure. However that kind of center exists in as grown octahedron structured stishovite. existing similarities in PL center between those materials allow underline role of octahedron structure forming such kind of center in all these materials.

5. Conclusions.

Performed investigations show that the luminescence center in stishovite, dense polymorph modification of silicon dioxide, exists in as grown single crystals. The luminescence spectrum

consists of two bands, a slow blue one at 3 ± 0.2 eV with main living time 17 μ s and a fast UV band at 4.7 ± 0.1 eV with living time 1.2 ns for thermally non-quenched intra center transitions. It discovered correlation between presence of OH group in the stishovite crystal and peculiarities in decay kinetics of the blue luminescence. A growth kinetics is observed and that is explained as motion of nearest OH group, which affects emitting properties of the center. The observed luminescence center in stishovite is very similar to the oxygen deficient center of luminescence silica glass and damaging radiation induced luminescence center of α -quartz crystal.

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