

Luminescence of silicon Dioxide – silica glass, α -quartz and stishovite*

Research Article

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Abstract:

This paper compares the luminescence of different modifications of silicon dioxide – silica glass, α -quartz crystal and dense octahedron structured stishovite crystal. Under x-ray irradiation of pure silica glass and pure α -quartz crystal, only the luminescence of self-trapped exciton (STE) is detected, excitable only in the range of intrinsic absorption. No STE luminescence was detected in stishovite since, even though its luminescence is excitable below the optical gap, it could not be ascribed to a self-trapped exciton. Under ArF laser excitation of pure α -quartz crystal, luminescence of a self-trapped exciton was detected under two-photon excitation. In silica glass and stishovite mono crystal, we spectrally detected mutually similar luminescences under single-photon excitation of ArF laser. In silica glass, the luminescence of an oxygen deficient center is presented by the so-called twofold coordinated silicon center (L.N. Skuja et al., Solid State Commun. 50, 1069 (1984)). This center is modified with an unknown surrounding or localized states of silica glass (A.N. Trukhin et al., J. Non-Cryst. Solids 248, 40 (1999)). In stishovite, that same luminescence was ascribed to some defect existing after crystal growth. For α -quartz crystal, similar to silica and stishovite, luminescence could be obtained only by irradiation with a lattice damaging source such as a dense electron beam at a temperature below 80 K, as well as by neutron or γ -irradiation at 290 K.

In spite of a similarity in the luminescence of these three materials (silica glass, stishovite mono crystal and irradiated α -quartz crystal), there are differences that can be explained by the specific characteristics of these materials. In particular, the nature of luminescence excited in the transparency range of stishovite is ascribed to a defect existing in the crystal after-growth. A similarity between stishovite luminescence and that of oxygen-deficient silica glass and radiation induced luminescence of α -quartz crystal presumes a similar nature of the centers in those materials.

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1. Introduction

Silicon dioxide exists in many polymorph modifications. They are α -quartz, cristobalite, stishovite and coesite. Polymorph modifications are based on the ability of silicon to undergo sp^3 hybridization and belong to a family of tetrahedron structured materials. An investigation of these modifications is of interest both for fundamental science and for applications in industry. Stishovite, a dense ($4.28 \text{ g}\cdot\text{cm}^{-3}$) octahedron structured polymorph modification has not been studied in sufficient depth yet, however, theoretical and experimental approaches of its study have now commenced and the first results have been obtained [1–5]. It is hard to believe that stishovite and α -quartz can be composed of the same elements in equal proportions, yet can be so different from each other by properties. The main element of the structure of dense silicon dioxide – stishovite, is based on another form of silicon hybridization – d^2sp^3 , providing an octahedral surrounding of the silicon with oxygen ions. Our interest is to study the changes in the electronic states and point defects that arise due to the transition from a tetrahedron structured modification to an octahedron structured modification of the silicon dioxide. We state that our knowledge of tetrahedron structured modifications of silicon dioxide is much more advanced than that for octahedron structured modifications, and therefore the latter needs more investigation. Examinations of electron states and point defects with optical methods are used widely, so we targeted those methods for octahedral silicon dioxide. Silica glass possesses the main element of the structure – a tetrahedron, however, it is important to bear in mind that a disordered structure of glass could be imagined as a density fluctuation. Achieving structures based on octahedrons, concentrated to some dense areas, requires further investigation.

Little is known about defects in stishovite. The role of hydrogen in the form of a OH group has been studied for a long time (see e.g. [6]). Bendeliani found that in Raman spectra there are no lines corresponding to the OH bond¹. In [6] it was found that IR spectra contain optical absorption bands corresponding to OH. The influence of iron and aluminum impurities on the OH IR absorption band intensity was studied. It was found that samples with and without iron possess a similar intensity of OH absorption, whereas an aluminum impurity can stimulate the intensity of OH IR absorption. Therefore, it was concluded that OH impurities could mainly be incorporated into a defect structure, host or impurity [6].

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

It was also found that luminescence of stishovite single crystal appears both in recombination and intra center processes [1, 3–5], and in ionizing or photo irradiation. Additionally, in the case of poly-crystals, the photoluminescence excitation spectrum was measured [2].

Previous research [7] of stishovite luminescence was not able to definitively answer the question of whether the luminescence center exists in the form of one of the three materials considered in this research, or if it was created with ionizing irradiation. To resolve this we investigated some virgin single crystals. There is no data for spectral photoluminescence – the kinetic behavior of the temperature range of liquid helium. Previously, the luminescence of only a single crystal sample was investigated; however, a generalization of the observed properties over the whole family requires data for many crystals and that aspect is covered in this work.

Also, in the past, it was noticed that luminescence of stishovite was very similar to that of oxygen deficient silica glass as well as of neutron, γ or dense electron beam irradiated α -quartz crystals [8–12]. This could confirm the presumption of the creation of octahedron motifs in the network of glass during preparation. Oxygen deficient luminescence of silica glass is connected to the so-called oxygen deficient center of luminescence (ODC), and several types of ODC have been distinguished in existing literature. The ODC with a relatively clear geometric and energetic model is the so-called ODC(II) or a twofold coordinated silicon. For that particular center, an absorption band is found centered at 5 eV, and two luminescence bands, a blue one at 2.7 eV and UV one at 4.4 eV can be excited [13]. The first band decays exponentially with a time constant $\tau = 10.3 \text{ ms}$ which is characteristic for triplet-singlet transitions. The second band decays with $\tau = 4.5 \text{ ns}$ and corresponds to singlet-singlet transitions in ODCs [13]. Beside the ODC(II) or twofold coordinated silicon, a wide spectrum of modified ODC is observed due to nearest defects, or in other words, ODCs forming a complex with nearest defects [14–17]. The parameters of such ODC luminescence are different from those of the lone twofold coordinated silicon center [13], however, PL spectra are similar to ODC(II). We will continue the lumines-

¹ N.A. Bendeliani, private communication

cence comparison of a stishovite mono crystal, (which is so small in size that it cannot be seen with the naked eye) with that of ODC in silica glass and irradiated α -quartz crystal.

2. Experimental procedure

The stishovite single-crystals were grown under hydrothermal conditions by methods published in [18, 19]. For our investigations, we used optically transparent single-crystals with dimensions of about $0.2 - 0.4 \times 0.6 \times 0.9 \text{ mm}^3$. The samples were kept on copper holders covered with an indium layer containing a hole, in which the samples were pressed to avoid gaps that could pass light through the sample. The excitation was made from one side of the holder and detection from the other, so that the possible luminescence of contamination on the surface of the holder was excluded. Pure silica glass samples of different manufactures as well as pure γ -irradiated and non-irradiated α -quartz crystals, studied in detail previously [7, 9–12], were used for comparison.

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

In these experiments, KrF, ArF and F_2 lasers (model PSX-100, made by Neweks, Estonia), as well as an x-ray tube, were used as luminescence excitation sources. The F_2 (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 fold higher power. The light of the F_2 laser was passed through a copper tube with a flow of nitrogen. The light of the KrF and ArF laser was incident on the sample through a layer of air. The excitation laser was situated at a distance of 1 m from the sample. The beam of the laser was $2 \times 2 \text{ mm}$. The crystalline silicon dioxide α -quartz, with a low level of luminescence, was used as a window to allow the light of the excitation lasers to pass through. The photoluminescence intensity of the studied samples had a linear dependence on excitation

intensity; therefore, the excitation regime was a single photon. Monitoring of the excitation intensity was realized with LiF crystal plates of different thicknesses, where the attenuation degree was determined with the use of a power-meter.

The x-ray tube contained a W-anticathode working in the regime 50 kV, 20 mA. Two cryostats were used. One of the cryostats maintained the temperature in the range of 60–400 K. The value of 60 K was achieved by pumping liquid nitrogen from the cryostat. Some measurements were realized with the use of a helium refrigerator. The temperature range in this case was 16–300 K. Luminescence detection was realized 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 path of luminescence detection. An oscilloscope (Textronic TDS 2022B) was exploited for decay curve registration. Each curve was averaged over 128 pulses. The time resolved spectra were measured by registration of the decay curve for each point of the PL spectrum in two time ranges – one in the ns range, and the other in the μs range. The measured curves are presented in figures as provided; therefore they reflect the level of errors. The discharge of excimer laser provides a strong stray current in the measurement circuit, which distorts the signal for a short time range.

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

3. Results

The optical absorption of the sample of stishovite single crystal being studied is presented in Fig. 1. Qualitatively, that spectra corresponds well to a previously measured smaller sample [3]. The spectrum on Fig. 1 and the previously measured spectrum [3] are similar with an intrinsic absorption threshold at 8.75 eV. The spectrum of stishovite is compared with that of silica glass, γ -irradiated and non-irradiated α -quartz crystals. The threshold of silica glass is situated at 8.2 eV with a well known band at 7.6 eV. Non-irradiated α -quartz crystal possesses an intrinsic absorption threshold at 8.5 eV for 290 K. γ -irradiated α -quartz crystal has an induced absorption band at 7.7 eV. It is presumed that the nature of this band in the as-received silica glass is similar to that in γ -irradiated α -quartz crystal [8–11]. The process of absorption in stishovite in the

range of 7.6 eV promises to possess similar characteristics, however, this needs a more detailed study.

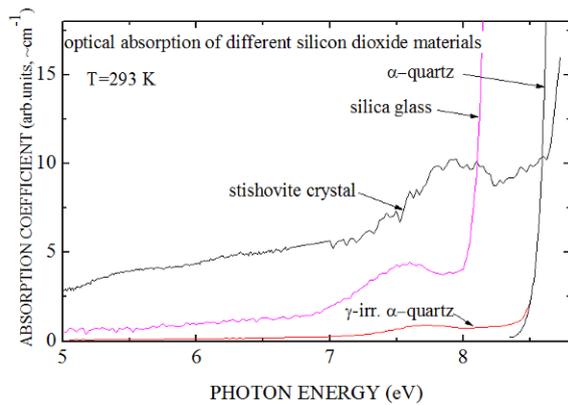


Figure 1. Optical absorption spectrum of the studied stishovite single crystal. Crystal size $0.2 \times 0.6 \times 0.9 \text{ mm}^3$ was too small for the correct determination of the absolute value of the absorption coefficient. Present data is presented in “arbitrary units” allowing for an estimate of the value of absorption coefficient. Also, the spectra of silica glass, γ -irradiated and non-irradiated α -quartz are in this figure, for which the absorption coefficient is given in cm^{-1} .

In addition, we measured the IR absorption of stishovite (Fig. 2). We have not had the opportunity to make the aperture for the reference beam to be the same size as the sample, so we could not determine the exact value of the absorption coefficient, so the data in Fig. 2 are presented in arbitrary values. However, the numbers are close to the absorption coefficient in cm^{-1} . The spectra of different samples are in mutual agreement, within the range of experimental error. The intrinsic absorption starts 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 $\alpha \sim 9.1 \text{ cm}^{-1}$; and a number of small bands at 3759 , 4001 and 4490 cm^{-1} . Comparison with data in literature [6] allows us to interpret the first two bands as being connected with the presence of hydroxyl (OH), therefore, the less intensive bands are possibly due to phonon side bands. The concentration of the hydroxyl group could be estimated on the basis of data [6] on the level of 20 wt ppm.

X-ray excited spectra of different polymorphs of silicon dioxide – silica glass, cristobalite, α -quartz and stishovite samples are presented in Fig. 3. For the first three samples, the presented luminescence bands belong to self-trapped exciton [20]. For dense tetrahedron structured coesite, STE-like luminescence was detected [1]. The case of pure, almost oxidized silica glass shows a spectrum which is close to that of cristobalite rather than to α -quartz. In such kind of silica glass the defect luminescence could be

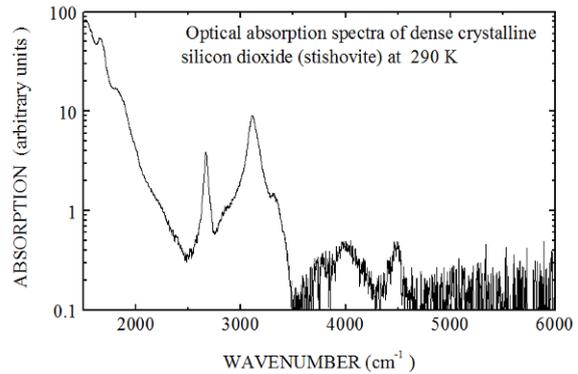


Figure 2. IR optical absorption spectrum of the stishovite single crystal at 290 K. The bands at 2668 cm^{-1} with FWHM 50 cm^{-1} and $\alpha = 3.8 \text{ cm}^{-1}$ and at 3111 cm^{-1} with FWHM 104 cm^{-1} and $\alpha = 9.1 \text{ cm}^{-1}$ are ascribed to the presence of OH- ions in concentration about 3000 ppm (according to [6]).

excited weakly with x-ray. The case of stishovite provides a completely different x-ray excited luminescence spectrum. Because such a luminescence of stishovite could be excited in the range below the optical gap, it could not be ascribed to STE. Consequently, the existence of STE should belong to tetrahedron related structures of silicon dioxide materials.

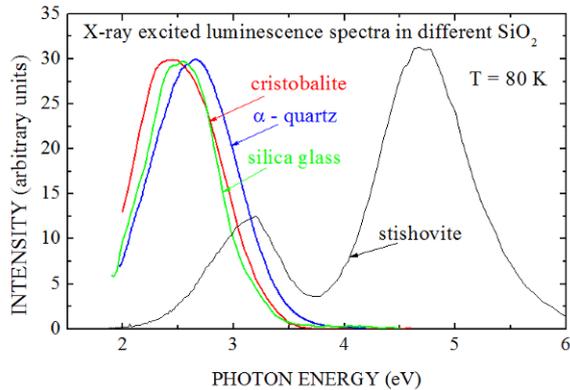


Figure 3. x-ray excited spectra of different silicon dioxide materials at 80 K. Cristobalite [20], α -quartz [20], pure silica glass [20], stishovite mono-crystal [1].

In Fig. 4, the photoluminescence spectra under ArF laser excitation are presented for silica glass, γ -irradiated, non-irradiated α -quartz and stishovite. In pure, non-irradiated α -quartz, only STE luminescence was obtained (the focusing lens for achieving a two-photon regime was used for the excitation of luminescence) [21], see curve 1, Fig. 4. For pure silica glass, γ -irradiated α -quartz and stishovite, two luminescence bands are observed, one in the blue range

and one in UV range of spectra. No focusing lens was used in these cases. The UV bands in all these last samples are fast. It is about 4.5 ns for silica glass under pulses of ArF laser [22] and 1.3 ns for γ -irradiated α -quartz under pulses of synchrotron [9–11]. A similar UV band could be induced in pure non-irradiated α -quartz crystal with a dense electron beam at temperatures below 80 K [12]. Details of stishovite luminescence are described below. The blue band of oxygen deficient silica glass possesses complicated decay kinetics [22, 23]. It undergoes exponential decay with a time constant of 10.3 ms at 290 K, a shorter non-exponential decay, and an intensity growth with cooling [23]. The blue band of γ -irradiated α -quartz possesses mainly fast kinetics of about 3 ns at low temperatures [10].

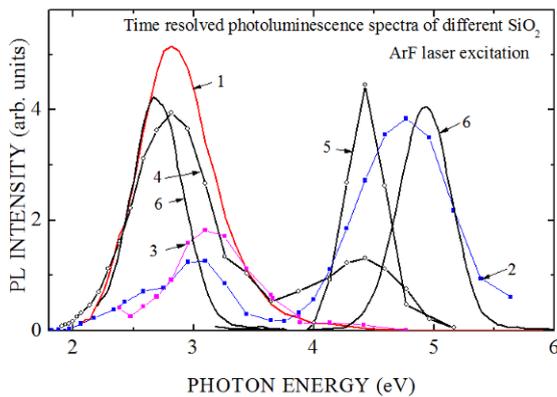


Figure 4. Time resolved photoluminescence spectra in different silicon dioxide materials. ArF laser (193 nm): 1 – two-photon excitation of α -quartz crystal at 12 K [21]; 2 – single-photon excitation of stishovite fast luminescence (~ 1 ns); 3 – single-photon excitation of stishovite slow luminescence ($\sim 17 \mu\text{s}$) at 12 K; 4 – single-photon excitation of oxygen deficient silica slow luminescence ($\sim 10 \mu\text{s}$) at 12 K; 5 – single-photon excitation of oxygen deficient silica fast luminescence (~ 5 ns) at 12 K. Synchrotron radiation: 6 – excitation of fast (~ 2 ns) luminescence of γ -irradiated α -quartz at 17 K [11].

Luminescence spectra of the stishovite virgin samples were studied under excitation of three excimer lasers (Fig. 5). These spectra are very similar for different samples. Generally, we observe two broad bands. One is in the blue part of the spectrum at 3 ± 0.2 eV with FWHM equal to 0.8 ± 0.2 eV. It is observed in all kinds of excitation regimes using 248; 193; 157 nm excimer lasers and under x-ray, as well. Another band is in the UV part of the spectrum with a peak at 4.7 ± 0.1 eV with FWHM equal to 0.95 ± 0.1 eV. While it was not observed under the 157 nm laser, a structure-less tail of the band in UV could be detected under 248 nm. This UV band is well observed under the 193 nm laser and x-ray irradiation. Cooling from 290 K

to 80 K and even to 16 K does not significantly affect the width of the bands. So the width of the bands is determined by other reasons than by homogeneous broadening.

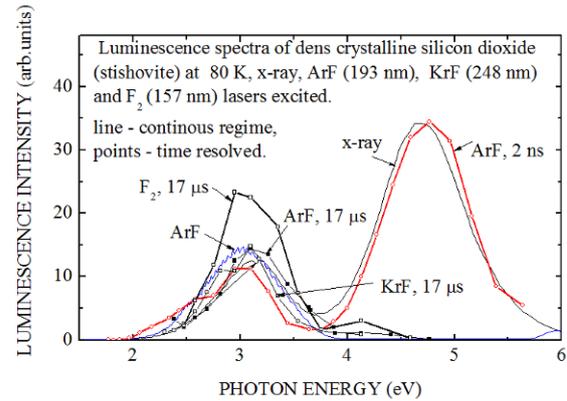


Figure 5. Photoluminescence excited with different excimer lasers (ArF (193 nm), KrF (248 nm) and F₂ (157 nm)) and x-ray excited luminescence spectra of stishovite single crystal sample at 80 K. Integration of decay curve of corresponding duration was performed to determine the intensity.

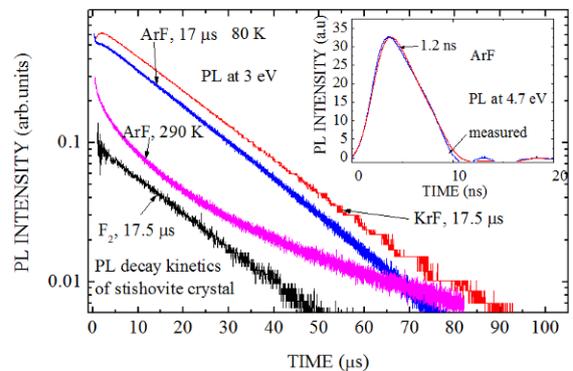


Figure 6. PL decay kinetics curves of stishovite single crystal excited with excimer lasers. Decay time constant of the blue luminescence is about $17 \mu\text{s}$, whereas the decay time for UV band is about 1.2 ns. Last estimation was made by comparing of measured kinetics curve with an exponential decay curve of 1.2 ns time constant convoluted with laser pulse shape.

The PL decay kinetics curves are presented in Fig. 6. The main part of decay of the blue PL is exponential with $\tau = 17 \pm 1 \mu\text{s}$ within a wide range of temperatures from 16 to 200 K, however, there are some peculiarities. First, at 290 K under ArF laser, we observe a strong non-exponential decay which becomes more exponential below 200 K. This could be explained with recombination luminescence additional to intra center excited luminescence.

Indeed, measurements with photon counting methods reveal decay in a longer time range, being strongly non-exponential and obeying a power law decay, Fig. 7.

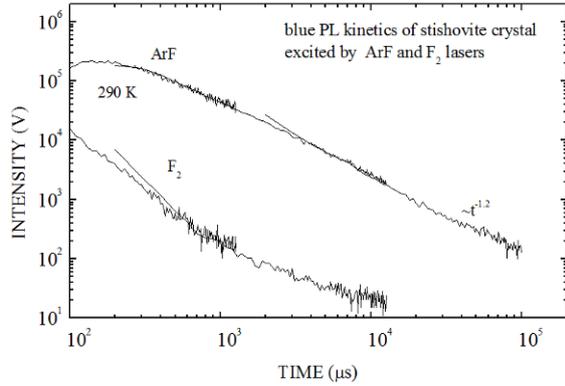


Figure 7. The blue PL decay kinetics of stishovite single crystal measured with the photon counting regime. Curves are measured in different time scales of an analyzer and sewed. A growth kinetic in the case of ArF laser excitation is related to the disability of fast luminescence detection in the photon counting regime, when single electron pulses of PMT are flowing together due to high intensity of excitation.

In addition to the main exponential decay of the blue PL with $\tau \sim 17 \mu\text{s}$ and power law decay of low intensity, we also observe a peculiarity in decay, manifesting itself as an intensity growth at about $5 \mu\text{s}$, Fig. 6. This is observed for excimer lasers excitation in all studied samples. It could not be connected with PM overload, because this growth is also obtained with diminishing of light intensity falling onto PM by narrowing the slits of the monochromator. The position of this growth is changed with temperature, Fig. 8. The energy activation of this thermally activated process is 0.031 eV and its corresponding frequency factor is about $5 \cdot 10^6 \text{ s}^{-1}$. The expression used for that is Mott's expression [24] for time constant:

$$\tau = \tau_o \left(1 + f \cdot \tau_o \exp \left(-\frac{E}{kT} \right) \right)^{-1}, \quad (1)$$

where τ_o time constant non affected by temperature, f – frequency factor, E – activation energy, T – temperature, k – Boltzmann constant.

The temperature dependences for the blue and UV PL parameters, determined from decay curves shown in Fig. 9 are presented in Fig. 9. We observe a correspondence between the PL intensity and decay time constants with temperature dependences. There is a similarity of dependences $\tau(T)$ and $I(T)$ for temperature ranges of 50–400 K.

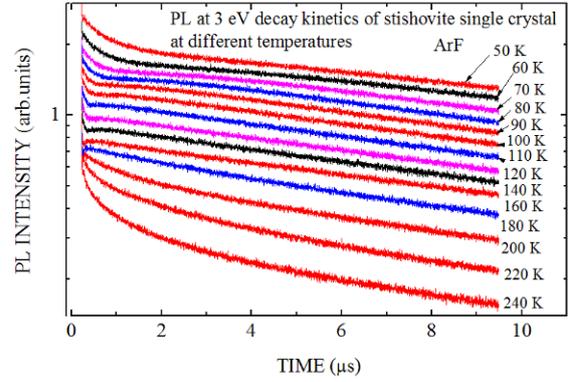


Figure 8. PL decay kinetics curves of stishovite single crystal excited with ArF excimer laser at different temperatures. The curves are multiplied by an arbitrary factor to separate them.

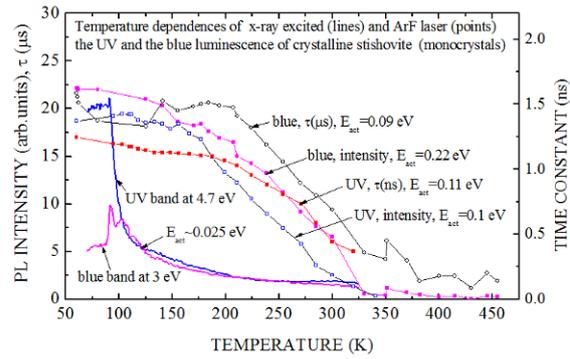


Figure 9. Temperature dependences of x-ray excited blue and UV band intensities, time resolved PL intensities (obtained by integrating the decay curves) and decay time constants of the principal part of decay excited with the ArF laser. The energies of thermal quenching are presented as well.

The temperature dependences of intensity for both x-ray excited bands, measured with the photon counting method are presented in Fig. 9. This data is compared with that of the time resolved intensity of the blue and UV PL as well as with time constant temperature dependences of both bands for stishovite single crystal excited with ArF laser. A strong effect was observed; in particular, a significant fall down in intensity of x-ray excited luminescence at 100 K does not correspond to changes in the thermal dependences of PL parameters. The parameters of thermal dependences were determined in accordance with Mott's law analogous to (1) already presented above for the time constant:

$$I(T) = I_o \left(1 + f \cdot \tau_o \exp \left(-\frac{E_a}{kT} \right) \right)^{-1}, \quad (2)$$

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 $E_a = 0.03 \pm 0.01$ eV. Frequency factors are $f(UV) = 10^{11} \text{ s}^{-1}$, $f(blue) = 10^7 \text{ s}^{-1}$, for the case of x-ray. $E_a = 0.15 \pm 0.05$ eV with frequency factors are $f(UV) = 10^{12} \text{ s}^{-1}$, $f(blue) = 10^9 \text{ s}^{-1}$ for the case of PL. So the processes of thermal quenching are different for these kinds of excitation.

4. Discussion

We have compared the luminescence of an as-grown single crystal – dense silicon dioxide polymorph modification – stishovite, with that of oxygen deficient silica glass and γ -irradiated α -quartz. Luminescence centers exist in non-irradiated samples of stishovite and similar luminescence was observed in silica glass and γ -irradiated α -quartz crystal. In pure, non-irradiated α -quartz crystal, no similar luminescence exists. Two luminescence bands in blue and in UV ranges are observed in all three of these samples. For stishovite, the blue band has a time constant of about 17 μs in the temperature range 16 – 200 K. Its long duration may be due to the forbidden transitions for intra-center process. The UV band is fast with τ of about 1.2 ns and it is due to allowed transitions. Both bands could also be excited in the recombination process. Both bands perform thermal quenching in the same temperature range, and therefore, could be ascribed to the same center.

As previously stated [1, 3–5, 7], we connect the luminescence of a single crystal of stishovite with similar luminescence (also two bands, blue and UV) in as-received oxygen deficient silica glass [13–17] and an analogous luminescence center in α -quartz crystal induced [9–12] with damaging radiation (γ , neutron and dense electron beam). That means similar defects are observed in these materials. However, the conditions of defects appear different for these materials. The defects exist in the as-grown crystals of stishovite, whereas the same are never observed in as-grown crystals of α -quartz. Hence the defects are inherent in the octahedron structure than in the tetrahedral. Damaging irradiation of α -quartz and density fluctuations during the silica glass preparation provides these defects. So, existing similarities in PL centers between those materials allow us to emphasize the role of octahedron structures in forming such kinds of centers in all these materials. Certainly, further investigations of the real structure of the defects, essentially in stishovite, are needed. The actual problem is the very small dimensions of the existing samples (e.g. a really small piece of sand), which does not allow for the use of advanced methods of

investigation such as ODMR, ESR, etc. The second problem is an insufficient quantity of the crystal. In spite of this, the luminescent method was sufficiently fruitful, however, the optical absorption, observed previously in the UV range and now in IR range, was informative.

The samples of stishovite possess OH groups that can be detected with IR absorption spectra measurements, see Fig. 2. The presented data are qualitative because the dimensions of the sample are too small for quantitative measurements of the absorption coefficient. As mentioned, OH groups in stishovite could be connected mainly with defects [6]² in general and, in our particular case, to defects providing the 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 a photolytic reaction for this complex, changing bonding and distances. Normally, an OH group, interacting with a luminescence center, provides a luminescence quenching effect in the case of many centers (see e.g. [25]). Removal of an OH group by absorption of photons activates the luminescence center [25]. Different distances of luminescence centers and separated OH groups could change populations on the excited state, modulating decay kinetics. Indeed, on the main decay kinetics curve for blue luminescence, besides the well-defined exponential decay with the mentioned time constant of 17 μs , we have that curve bending with a component of growth in a time range of μs units that is far away from the excitation pulse. The nearest OH group could affect its life time on the excited state.

The effect of a strong fall down at 100 K in x-ray and the lack of such a decrease in the intensity of PL at that temperature could be explained by differences of OH interaction of centers making radiation transitions in the intra center process and the recombination process. X-ray luminescence appears mainly in the recombination process. Probably, the OH groups are participating in charge trapping, providing competitive trapping of charge and then diminishing of luminescence intensity. Perhaps the OH group should be separated from the center and the value of 100 K is a threshold of the OH group motion in the studied material. Above 100 K, the OH group easily comes back to the center and quenches the luminescence.

ODC luminescence of silica glasses, with which we compare the luminescence of stishovite, is well studied for dry silica (see for example [13–16]), therefore a one-to-one correspondence is not possible because of the OH group's influence on the crystal. On the other hand, there is a

² N.A. Bendeliani, private communication

significant difference in the OH group's incorporation into silica glass and crystals. In the crystals, the OH groups are in the form of interstitials; in silica glass, the main OH position is to be incorporated in the glass network as Si-O-H. Therefore, there is no possibility for a one-to-one comparison of the studied luminescence centers in OH containing stishovite and wet silica glass.

5. Conclusions

Investigations conducted demonstrate that the luminescence center in stishovite, a 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 a main life time of $17 \mu\text{s}$ and a fast UV band at 4.7 ± 0.1 eV with a life time 1.2 ns for thermally non-quenched intra center transitions. A correlation between the presence of an OH group in the stishovite crystal and peculiarities in decay kinetics of the blue luminescence is discovered. Growth kinetics are observed and explained as the motion of the nearest OH group, which affects the emitting properties of the center. The observed luminescence center in stishovite is very similar to the oxygen deficient center of luminescence silica glass and to the damaging radiation induced luminescence center of α -quartz crystal. It is demonstrated that the luminescence of stishovite single-crystals exists in as-grown, non-irradiated samples. The correlation of the properties of luminescence in stishovite and silica glass could show that octahedron motifs are possible in the network of silica glass. Irradiation with the damaging source of α -quartz crystal could provide compaction areas with a luminescence center similar to stishovite.

Acknowledgments

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References

- [1] A.N. Trukhin, J.L. Jansons, T.I. Dyuzheva, L.M. Lityagina, N.A. Bendeliani, *Solid State Commun.* 127, 415 (2003)
- [2] A. Paleari, N. Chiodini, D. Di Martino, F. Meinardi, P. Fumagalli, *Phys. Rev. B* 68, 184107 (2003)
- [3] A.N. Trukhin, J.L. Jansons, T.I. Dyuzheva, L.M. Lityagina, N.A. Bendeliani, *Solid State Commun.* 131, 1 (2004)
- [4] A. Trukhin et al., *Phys. Status Solidi C* 2, 584 (2005)
- [5] A.N. Trukhin, T.I. Dyuzheva, L.M. Lityagina, N.A. Bendeliani, *J. Phys.-Condens. Mat.* 20, 175206 (2008)
- [6] K.D. Litasov et al., *Earth Planet. Sc. Lett.* 262, 620 (2007)
- [7] A.N. Trukhin, *J. Non-Cryst. Solids* 355, 1013 (2009)
- [8] C.M. Gee, M. Kastner, *J. Non-Cryst. Solids* 40, 577 (1980)
- [9] M. Cannas, S. Agnello, R. Boscaino, F.M. Gelardi, A. Trukhin, *Radiat. Meas.* 38, 507 (2004)
- [10] M. Cannas, S. Agnello, R. Boscaino, F.M. Gelardi, A. Trukhin, *Phys. Status Solidi C* 4, 968 (2007)
- [11] M. Cannas et al., *J. Phys.-Condens. Mat.* 16, 7931 (2004)
- [12] A. Trukhin, P. Liblik, C. Lushchik, J. Jansons, *J. Lumin.* 109, 103 (2004)
- [13] L.N. Skuja, A.N. Streletsky, A.B. Pakovich, *Solid State Commun.* 50, 1069 (1984)
- [14] A. Truhins, L. Skuja, A. Boganovs, V. Rudenko, *J. Non-Cryst. Solids* 149, 96 (1992)
- [15] A.N. Trukhin, H-J. Fitting, *J. Non-Cryst. Solids* 248, 49 (1999)
- [16] A.N. Trukhin, In: G. Pacchioni, L. Skuja, D.L. Griscom (Eds.), *Defects in SiO₂ and Related Dielectrics: Science and Technology* (Kluwer Academic, London, 2000) 235
- [17] A.N. Trukhin, J. Troks, D.L. Griscom, *J. Non-Cryst. Solids* 353, 1560 (2007)
- [18] L.M. Lityagina, T.I. Dyuzheva, N.A. Nikolaev, N.A. Bendeliani, *J. Cryst. Growth* 222, 627 (2001)
- [19] T.I. Dyuzheva, L.M. Lityagina, N.A. Bendeliani, N.A. Nikolaev, *Kristallografiya* 43, 554 (1998) (in Russian)
- [20] A. Trukhin, A. Plaudis, *Sov. Phys.-Sol. State* 21, 644 (1979)
- [21] A.N. Truhins, M. Kink, J. Maksimov, R. Kink, *Solid State Commun.* 127, 655 (2003)
- [22] A.N. Trukhin, J. Teteris, A. Fedotov, D.L. Griscom, G. Buscarino, *J. Non-Cryst. Solids* 355, 1066 (2009)
- [23] A.N. Trukhin, A. Sharakovski, J. Grube, D.L. Griscom, *J. Non-Cryst. Solids* 356, 982 (2010)
- [24] D. Curie, *Luminescence in Crystals* (Wiley, New York, 1963)
- [25] I.A.A. Terra, A.S.S. de Camargo, M.C. Terrile, L.A. Nunes, *J. Lumin.* 128, 891 (2008)