Luminescence of rutile structured crystalline silicon dioxide (stishovite)

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Luminescence spectrum of synthetic mono-crystalline stishovite comprises a slow blue band at ~400 nm (~3.1 eV) and a fast UV band at ~260 nm (~4.7 eV), as well as some bands in near-infrared range of spectra. The NIR luminescence of stishovite crystal, excited with lasers 532 nm, 248 nm and 193 nm as well as x-ray, possesses several sharp lines. A zero phonon line is situated at 787 nm (1.57 eV) and grows with cooling. An anti-Stokes line is located at 771 nm (1.68 eV). This line disappears with cooling. In a powder sample of stishovite created by shock waves generated by the impact of a 50-m-diameter meteorite in Arizona 50,000 years ago, the PL broad blue band is situated at 425 nm (2.9 eV), the UV band at ~260 nm (~4.7 eV), and the sharp lines, seen only under 193 nm laser, at 689 nm (1.789 eV), 694 nm (1.785 eV) and 706 nm (1.754 eV). We ascribe the fast UV luminescence to singlet–singlet transitions and the slow blue band to triplet–singlet transitions of the same intrinsic defect of stishovite in both types of samples. The blue band in stishovite crystal exhibits delayed luminescence of recombination nature, whereas the blue band of Arizona's powder sample does not exhibit such effect. This difference is explained by different surroundings of luminescence center in those samples. NIR luminescence of mono-crystalline stishovite is ascribed to carbon impurity penetrated in the sample from graphite heater. NIR luminescence of powder from Arizona has not yet found an explanation.

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1. Introduction

Here we are continuing an investigation on dense crystalline silicon dioxide (stishovite) by luminescence methods which were started in our previous works [1–6]. A significant property of stishovite is the octahedral coordination of silicon and the three-fold coordination of oxygen therefore possessing rutile structure. Previously we had found that stishovite single crystals possessed two luminescence bands: a blue one at ~400 nm (~3.1 eV) and a UV one at ~260 nm (~4.7 eV) [1–6], both excitable in the range below optical gap (8.75 eV) [2] of stishovite. An intra-center mechanism of luminescence was established [4]. The blue band decay kinetics could be well approximated by an exponential at low temperatures (~80 K) having \( r = 17.5 \mu s \), whereas the UV band is fast, having \( r = 1–2 \) ns. An interesting effect was observed on decay of the blue luminescence [46], i.e., some period of deviation from monotone decay and even the increase in intensity that superimposed on the decay curve. This effect exhibits a dependence on temperature [6]. It is shown as a thermally delayed luminescence. According to the paper [7] three types of delayed luminescence are distinguished: (1) E-type related to feeding of singlet state from triplet one, (2) P-type of feeding of singlet state from two triplet states, and (3) recombination delayed luminescence. Emitting level is populated by the recombination of charges which are trapped on the nearest defect. In the case of stishovite the mono-crystal luminescence could be interpreted as recombination delayed luminescence.

Previously we had attributed both luminescence bands to a single defect, the nature of which is similar to the known oxygen deficient centers (ODCs) present in silica glass [5,8]. Remarkably, this luminescence center does not exist in crystalline \( \alpha \)-quartz. However, destructive irradiation of \( \alpha \)-quartz crystals with fast neutrons, \( \gamma \) rays, or dense electron beams [9,10] creates luminescence centers very similar to that of stishovite. In stishovite the blue band decays faster than similar bands in oxygen deficient silica glass and slower than those in \( \gamma \)-irradiated \( \alpha \)-quartz [11]. These stishovite bands were attributed to triplet–singlet transitions, as in the case of ODC(II) in silica; however were affected with different surroundings of the defect.

Two types of ODCs are distinguished in silica glass. One of them is SiODC(II) of oxygen deficient silica glass for which a well-founded model was established. It is found to be two-fold coordinated silicon, where dangling p bonds are responsible for electronic transitions [12,13]. Another type is SiODC(I) which was described in many papers, see e.g. [14–17]; however no generally accepted model was
proposed for it. Some researchers ascribe it to the Si–Si bond or oxygen vacancy [17]. That contradicts with the absence of SiODC (I) defect in pristine α-quartz crystal [16]. We are proposing for SiODC(I) as a model of complex defect, which includes the two-fold coordinated silicon in the latent state surrounded with different host defects and an impurity [8]. Investigation of stishovite luminescence allows us to assume stishovite-like motives in the structure of SiODC(I).

One of the tasks of this investigation is the comparison of the luminescence properties of a synthetic stishovite single crystal to those of stishovite created by shock waves emanating from the impact of a giant meteorite striking the Earth 50,000 years ago and creating what is now known as the Meteor Crater, Arizona. Impacts of this large generated pressures of > 100 GPa and temperatures of > 2500 °C at the point of impact causes the vaporization of the impacted rocks [18]. The fact that the Meteor Crater sample is a powder suggests that it was formed as a condensate from a vapor phase. Another task is to check whether the UV luminescence of stishovite can be excited under 7.9 eV photons. In previous experiments [4,6] we failed to detect the UV luminescence of stishovite. The third task of this investigation is the search of new luminescence bands in stishovite. One band in the near-infrared range was previously detected [19], but it was neither investigated in the detail nor described in the previous publications.

2. Experimental procedure

Single crystals of stishovite have been grown from hydrothermal solution in the system SiO$_2$–H$_2$O under a pressure of 9–9.5 GPa within a temperature range of 1170–770 K [20]. Hereafter in the present paper it will be referred to as stishovite crystal. Natural quartz crystal powder was taken as the raw material. So, incorporation of impurities of natural quartz into stishovite synthetic crystal is possible. However, during production crystallization purification could also take place resulting in the decrease of impurities in synthetic stishovite compared to initial natural quartz powder. The crystals were grown in a platinum container directly in contact with a graphite heater. The graphite heater is a source of carbon impurities present in stishovite crystal. The samples of investigation were small, optically transparent single-crystals with the dimensions of about 0.2–0.4 × 0.6 × 0.9 mm$^3$. The samples were put on copper holders covered with an indium layer containing a hole into which the samples were forced in, avoiding the slits to let any stray light through. The excitation was done from one side of the holder and detection from the other, thus excluding irrelevant luminescence from possible contamination on the surface of the holder.

Another studied sample was stishovite produced by shock-waves taken from Meteor Crater, Arizona. Hereafter in the present paper it will be called stishovite powder. It was found in a powder form. Previously the defects of this sample were studied in [21] and cathodoluminescence in [22]. We pressed the powder into a plate covered with indium. The dimensions of such sample surface were about 8 × 8 mm$^2$.

Luminescence measurement details are described in [1–6]. The measured curves are presented in the figures as recorded; therefore they reflect the level of errors. The fact that discharge of the exciting excimer laser can give rise to strong stray currents in the measurement circuit is taken into account, which distorts the signal in the short-time range.

IR spectra of the stishovite powder were measured with a FTIR spectrometer Vertex 80v Bruker. The absorption spectrum was estimated from the measurements of diffuse reflectance.

3. Results

Photoluminescence (PL) spectra of a stishovite crystal under excitation of ArF laser pulses are presented in Fig. 1. We observe the blue luminescence and luminescence in near-infrared (NIR) by means of a Hamamatsu CCD mini-spectrometer. The NIR band contains several sharp lines. The blue and NIR luminescence of stishovite crystal can also be excited with the KrF laser (248 nm). These data are not shown in Fig. 1. If luminescence is detected with CCD mini-spectrometer the UV band is seen like a shoulder. However, it was possible to determine very well the UV band intensity by integrating the decay curves shown in Fig. 2. Before integration we have subtracted the decay curve recorded at 220 nm, where only the induced signal due to stray current is expected. The time constant of UV luminescence is around 0.5 ns within the luminescence band for 157 nm F$_2$ laser excitation. Determination of the decay time constants was performed using the shape of the laser pulse. Then the pulse shape was convoluted with exponentials of different time constants, and the convoluted

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**Fig. 1.** (Color online) Photoluminescence spectra of stishovite single crystal measured under excitation with ArF laser (193 nm) pulses. Line corresponds to spectrum measured with Hamamatsu CCD mini-spectrometer. Close points correspond to time resolved spectra, where intensity was determined by integration of decay curve measured at given wavelength. Points labeled “fast” are related to time range about some ns, whereas those labeled “slow” are related to time range of 10 μs. Accordingly open points correspond to time constant values obtained by extrapolation of decay curve with exponents. Data labeled “NIR” are measured with infrared sensitive photomultiplier.

**Fig. 2.** (Color online) Time resolved PL spectra of a stishovite single crystal and natural shock-created stishovite powder from the Meteor Crater, Arizona under excitation of F$_2$ (157 nm) laser in ns range of time. Close points correspond to time resolved spectra, where intensity was determined by integration of decay curve measured at a given wavelength. Open points correspond to time constant determined at 10 K.
curves were superposed on the measured luminescence decay curve.

Using the same procedure we measured the UV luminescence band of the stishovite powder, Fig. 2. It is located within experimental error in the same spectral position as in stishovite crystal. The approximated decay time constant is higher than that for the stishovite crystal and is on the level of 3 ns.

Detection of time constants for longer duration was performed by approximation of the measured decay curves as exponentials. The time resolved blue band in the range of 330–750 nm has a time constant on the level of 17 μs (Fig. 1). A tail of this PL band that is detected from 550 nm to 800 nm has the same time constant as the main blue band. In stishovite crystal similar decay of the blue luminescence is observed under excitation with the KrF laser. The time resolved spectrum of the NIR luminescence was measured with a poor resolution because of its low intensity; as a result the time resolved spectrum is taken as the contour of NIR luminescence measured with CCD in Fig. 1. The decay time is slow; the decay constant varies in 400–800 μs range within the experimental error.

The PL spectra of the stishovite crystal and the stishovite powder are compared in Fig. 3. It is seen that there are differences in positions of the blue band and the NIR luminescence for these two materials. The NIR PL lines of the stishovite powder are situated at 689 nm (1.789 eV), 694 nm (1.785 eV) and 706 nm (1.754 eV), see Fig. 3. In contrast to the case of stishovite crystal, where the NIR luminescence is excited by both ArF and KrF lasers, in the stishovite powder this luminescence is not observed under excitation with the KrF laser – see Fig. 3. That could be indicative of the different nature of the NIR luminescence in the studied samples. Decay parameters of the NIR luminescence of the stishovite powder were not yet measured.

The measured decay kinetics curves are presented in Fig. 4. It is seen that decay kinetics of stishovite mono-crystal is sufficiently well described with an exponent with time constant about 17 μs. Besides, in the beginning stage of decay we have observed some peculiarities, which are shown in the inset in Fig. 4. Such behavior was also studied previously [6]. It was found that the shapes of these peculiarities are temperature dependent.

We have measured decay kinetics of the blue and UV bands of the stishovite powder and found their difference from the corresponding data of the stishovite crystal. At low temperature the decay of the stishovite powder luminescence remains non-exponential under ArF and KrF lasers excitation, providing similar decay curves. The blue band's decay at 290 K is non-exponential both in the stishovite powder and stishovite crystal, Fig. 4.

However for stishovite crystal the decay in the late stage is close to 17 μs, whereas for stishovite powder it is faster than 17 μs and at the end of decay it could be approximated by a value of about 9 μs for the case of KrF laser (248 nm) and 6 μs for the case of ArF laser (193 nm) excitation. While the blue band of stishovite crystal exhibits a rise in intensity after the excitation pulse ceases (see Fig. 4 inset), no analogous effect of luminescence decay was observed under excitation with both lasers for the case of the stishovite powder neither at 290 K nor at 80 K (see Fig. 4 inset).

The UV band's decay is about 1 μs for the case of KrF laser (248 nm) and 32 ns for the case of ArF laser (193 nm) excitation for stishovite powder. So the UV band decay is slower in single crystal for the case of ArF laser (193 nm) excitation.

The NIR part of PL spectra of the stishovite crystal at different temperatures is presented in Fig. 5. The line at 771 nm is absent at 80 K, and thus it may be ascribed to an anti-Stokes transition, whereas the sharp line at 787 nm may be a zero phonon line. Its intensity increases with cooling. The NIR luminescence of stishovite single crystal could be also excited with 157, 193, 248, and 532 nm lasers, under x-ray excitation in a wide range of temperatures from 8 K to 450 K. For stishovite powder the NIR luminescence was observed only under ArF laser excitation with position of lines shifted relatively to the case of stishovite crystal.

The IR spectra of the samples under comparison are presented in Fig. 6. The intrinsic IR bands coincide mutually. Also the bands in the range of OH absorption exist, and in the case of stishovite powder the bands are broader and more intensive. This means that the concentration of OH groups in Meteor Crater stishovite is much higher.
Besides the IR absorption spectra we have measured the Raman spectra of the studied samples. Two lasers were used with emissions of 532 nm and 740 nm. For stishovite crystal the line at 757 cm$^{-1}$ was obtained using each of the lasers in spite of the broad and intense background. For stishovite powder we did not observe any line on the intensive background.

In Fig. 7 the PLE of the blue band is compared with the absorption spectrum for stishovite crystal. The PLE of the blue band is observed in the range of 5–11 eV. The PLE of the UV band was not possible to measure due to its low intensity. It could be assumed that the PLE of the UV band should be similar to that of the UV band.

4. Discussion

We report the comparison of properties between stishovite crystal and the stishovite powder. We have found similarities and some differences between these materials.

The IR absorption spectra presented in Fig. 6 show good similarity in the spectrum on the threshold of intrinsic vibration in the range below 2000 cm$^{-1}$. Spectra related to presence of water and OH groups are different, exhibiting difference in properties of these impurities in these materials.

The photoluminescence of the stishovite powder contains two bands: one in the blue range and another in the UV range, similar to stishovite crystal. The band in the UV range is not effective in the steady state excitation regime even for stishovite crystal. Previously [4] we were not able to distinguish the UV luminescence for stishovite crystal excited by F$_2$ laser, because of a strong influence of stray current due to the laser discharge. Now, using the procedure of subtracting the stray current decay curve we were able to extract fast decay kinetics from the total noisy curve and obtain the time-resolved UV band of a stishovite for excitation at 7.9 eV – just below optical gap (8.75 eV) for both the stishovite crystal and the stishovite powder. The UV bands possess similar position within experimental errors – see Fig. 2 – and decay of the UV bands is fast in both materials. However, values of time constant are different for the case of F$_2$ (157 nm) laser excitation. Probably, the nearest defects deactivate the corresponding emitting level of the center differently in those materials.

The blue bands of studied samples possess different positions. The blue band of stishovite powder is shifted to a higher wavelength (Fig. 3). The blue band decay kinetics at 290 K is non-exponential, (Fig. 4) for both materials. At 80 K the decay of the blue band of stishovite powder is significantly non-exponential, whereas for stishovite crystal it is exponential with time constant 17 µs. The blue band of the last material possesses a growth, shown in the inset in Fig. 4, which is absent for the case of stishovite powder.

Measurements of the blue band photoexcitation spectra were performed only for the small stishovite crystal. The obtained spectra include a range of intra-center excitation from 5 eV up to optical gap (8.75 eV) and the range above the optical gap, where defect excitation is due to transport of energy absorbed by host material atoms.

New luminescence bands with fine structure were observed for both samples in the near-infrared range (NIR) of spectra. The NIR spectra are different in stishovite crystal and stishovite powder. The nature of the fine structure could be due to the presence of some impurity ions providing narrow-line emission (rare earth ions, chromium, etc.) even at 290 K. However, rare earth solubility even in silica glass is limited [24]. We did not find any data about rare earth doped silicon dioxide crystals. Another possibility is the presence of carbon impurity in stishovite crystals creating a diamond-like defect under high pressure of synthetic stishovite crystal growth. A graphite heater used for growing the stishovite crystal [20] could be a source of carbon penetration in the crystal. In diamond the fine structure of luminescence bands, observed even at 290 K, is related to the presence of lattice defects and impurities [23]. In stishovite crystal carbon could create analogous to the diamond center possessing neighbor silicon, oxygen and defects of stishovite structure. It means that some carbon-related molecular defect occurs in stishovite crystal as an interstitial defect.

In the stishovite powder the position of the NIR bands is different to that in synthetic stishovite crystal, being situated at 689 nm (1.789 eV), 694 nm (1.785 eV) and 706 nm (1.754 eV). Here also the NIR luminescence could not be excited with KrF laser. So, there is not enough data for the assignment of the NIR bands of stishovite powder to carbon.

Let us consider correspondence of properties of the studied luminescence defect in stishovite and presumably relative defects in oxygen deficient silica glass [12–17] and neutron or γ-irradiated α-quartz crystal [9–11]. In all the three cases of silicon dioxide in different modifications there are similar luminescence centers. Besides, in all cases of the slow blue and fast UV luminescence bands there is the common fundamental property such as singlet–triplet splitting, which is similar for all three materials. The magnitude of singlet–triplet splitting could be estimated from energy difference of the blue and UV luminescence bands, which constitutes about 1.5 eV for all three materials. This could be considered as a sufficiently big split provided that the corresponding wavefunction is confined in...
This defect resembles SiODC(I) defect of oxygen deficient silica glasses which are excited with 157 nm laser. The center in stishovite, possessing luminescence at blue band, is slow and could be ascribed to singlet transitions in a luminescence center, correspondingly. In silica KrF efficiently excites the UV band. Otherwise under excitation of 157 nm with F2 laser, corresponding to absorption band of SiODC(I) defect, situation in silica and stishovite is similar. In both the cases UV band is excited with low efficiency.

The defect in stishovite could be excited in the recombination process. In silica glass SiODC(II) could not be excited in the recombination process, whereas SiODC(I) could [15,16]. Contrary to the case of oxygen deficient silica glass [15], in stishovite the UV band dominates in x-ray excited luminescence, while the blue one prevails in photoluminescence.

5. Conclusions

The photoluminescence of the impact-created Meteor Crater stishovite powder is found to have some differences and some similarities with those of our synthetic stishovite mono-crystal. Similarities are in the presence of the UV, blue and NIR luminescence bands. The UV luminescence is fast but the blue luminescence is slow and could be ascribed to singlet–singlet and triplet–singlet transitions in a luminescence center, correspondingly. Differences are in spectral positions of corresponding bands and different luminescence decay parameters, which need further investigation. The center in stishovite, possessing luminescence at blue and UV range of spectra, could be also excited with 157 nm laser. This defect resembles SiODC(I) defect of oxygen deficient silica glass and γ or electron beam irradiated α-quartz crystal. Similar values of singlet triplet splitting at ∼1.5 eV prove that these are related defects in silicon dioxide of different modifications.

We have discovered a defect in stishovite providing NIR luminescence of synthetic stishovite mono-crystal. This defect is ascribed to carbon impurity introduced in crystal from the graphite heater during growth. Actually, there is not enough data for analogous interpretation of NIR luminescence of the impact-created Meteor Crater stishovite.

Interaction of intrinsic defect, responsible for the UV and blue luminescence of stishovite, with carbon related quasimolecular defect and interstitial OH groups is the cause of delayed blue luminescence.

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