



# Luminescence of polymorphous SiO<sub>2</sub>



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## HIGHLIGHTS

- Luminescence of polymorphous silicon dioxide was studied.
- Raman spectra are different for quartz, coesite, stishovite, cristobalite and silica glass.
- Luminescence comprises bands of self-trapped exciton and host material defect.
- Luminescence of self-trapped exciton possesses high energetic yield for tetrahedron structured crystals.
- Defect related luminescence observed in silica glass as grown stishovite, coesite and irradiated quartz crystal.

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## ABSTRACT

The luminescence of self-trapped exciton (STE) was found and systematically studied in tetrahedron structured silica crystals ( $\alpha$ -quartz, coesite, cristobalite) and glass. In octahedron structured stishovite only host material defect luminescence was observed. It strongly resembles luminescence of oxygen deficient silica glass and  $\gamma$  or neutron irradiated  $\alpha$ -quartz. The energetic yield of STE luminescence for  $\alpha$ -quartz and coesite is about 20% of absorbed energy and about 5(7)% for cristobalite. Two types of STE were found in  $\alpha$ -quartz. Two overlapping bands of STEs are located at 2.5–2.7 eV. The model of STE is proposed as Si–O bond rupture, relaxation of created non-bridging oxygen (NBO) with foundation of a bond with bridging oxygen (BO) on opposite side of **c** or **x,y** channel. The strength of this bond is responsible for thermal stability of STE. Similar model of STE was ascribed for coesite and cristobalite with difference related to different structure. STE of Silica glass is strongly affected by disordered structure.

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## 1. Introduction

SiO<sub>2</sub> exists in several polymorphous modifications built up of SiO<sub>4</sub> tetrahedral units as in  $\alpha$ -quartz (~2.65 g/cm<sup>3</sup>), coesite (~3 g/cm<sup>3</sup>) and cristobalite (~2.32–2.36 g/cm<sup>3</sup>) and of SiO<sub>6</sub> octahedral units as in stishovite (~4.3 g/cm<sup>3</sup>) with rutile structure.

The manifestations of self-trapped exciton (STE) were discovered in tetrahedron structured  $\alpha$ -quartz, cristobalite, coesite and silica glass (Griscom, 1979; Trukhin and Plaudis, 1978, 1979; Trukhin, 1987, 1978; Trukhin et al., 2015). STE was studied in details for  $\alpha$ -quartz, coesite, cristobalite and silica glass. The luminescence of STE in these materials is very effective essentially under ionizing radiation excitation. The energetic yield of the STE luminescence in pure crystal is about 20% of absorbed energy. Moreover,

the STE luminescence prevails the impurity luminescence in natural crystals. In stishovite the STE was not found; however, defect luminescence was observed in (Trukhin et al., 2003).

In silica glass STE luminescence and oxygen deficient defect related luminescence were observed. STE of silica glass is strongly affected with disorder and it may correspond for many structural elements (Trukhin, 1992).

The interpretation of defect related luminescence of silica was done on the model of oxygen deficient centers (ODC) (Skujia et al., 1984; Trukhin and Fitting, 1999). The ODC(II) or twofold coordinated silicon and ODC(I) are distinguished. ODC(I) is object of controversial interpretation. The Si–Si oxygen vacancy (Hosono et al., 1991) and complex defect including latent twofold coordinated silicon (Trukhin and Fitting, 1999) are proposed. Remarkably, this luminescence center does not exist in as grown crystalline  $\alpha$ -quartz. However, destructive irradiation of  $\alpha$ -quartz crystals with fast neutrons,  $\gamma$  rays or dense electron beams (Gee and Kastner, 1979; Cannas et al., 2004; Trukhin et al., 2004) creates ODC(I) like

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defect.

Stishovite and coesite exhibits luminescence similar to oxygen deficient silica glass as well as irradiated  $\alpha$ -quartz.

In this paper, we present short review of host material luminescence for different polymorphs of silicon dioxide with try overview common and different properties.

## 2. Experimental

High purity  $\alpha$ -quartz, pure silica glass of KS-4V and KY-1 types with different level of oxygen deficiency, synthetic stishovite single crystal and synthetic coesite single crystal were studied. The sample of cristobalite is intermediate product of pure silica glass KS-4V preparation (Boganov et al., 1974; Cheremisin et al., 2004). Silicon dioxide powder was crystallized in the presence of catalyst (Li), which was later washed out with chlorine. Chlorine was washed out with oxygen. Thus obtained ceramic-like polycrystalline sample was characterized by Raman spectroscopy. Its Raman spectrum under 532 nm cw laser excitation contains mainly lines of cristobalite (Kingma and Heymley, 1994) and also small amount of coesite (Gillet et al., 1990) (Fig. 1). The result shows that cristobalite phase dominates in the ceramics, which contains also some amount of coesite phase.

Single crystals of stishovite were grown from hydrothermal solution in the system  $\text{SiO}_2\text{--H}_2\text{O}$  under a pressure of 9–9.5 GPa within a temperature range of 1170–770 K, whereas coesite under pressure 4.5 GPa (Lityagina et al., 2001). The  $\alpha$ -quartz crystal sample was cut for dimension corresponding to that of stishovite and coesite 0.2–0.4–0.6–0.9 mm<sup>3</sup> therefore energetic yield for coesite and stishovite luminescence could be estimated. Others details of experiment could be found in (Trukhin and Plaudis, 1978, 1979; Trukhin, 1987, 1978; Trukhin et al., 2015, 2003).

## 3. Results

### 3.1. Silica glass

#### 3.1.1. ODC(II) or twofold coordinated silicon

In silica glass with high level of oxygen deficiency (Skuja et al., 1984) the two band luminescence center could be excited in the range of 5 eV (KrF laser for example) 6.4 eV (ArF laser) and 7.9 eV ( $\text{F}_2$  laser).

In the range of 5 eV the ODC(II) or the twofold coordinated

silicon center is excited through singlet–singlet transitions ( $^1\text{S}_1 \leftarrow ^1\text{S}_0$ ) (Skuja et al., 1984). Emission of UV band at 4.4 eV ( $^1\text{S}_1 \rightarrow ^1\text{S}_0$ ) is with time constant about 4.5 ns (Skuja, 1998). The blue emission at 2.7 eV is due to triplet–singlet ( $^3\text{T}_1 \rightarrow ^1\text{S}_0$ ) transitions (exponential decay, rare for glasses) with time constant about 10 ms (Skuja et al., 1984; Skuja, 1998). Population of the triplet state is due to  $^1\text{S}_1 \rightarrow ^3\text{T}_2 \rightarrow ^3\text{T}_1$  (Skuja, 1998). The UV bands time constant is little changed only from 4.6 ns to 4.1 ns (Nishikawa et al., 1994; Boscaino et al., 1996) with temperature in spite of the transition  $^1\text{S}_1 \rightarrow ^3\text{T}_2$  is thermally activated (Skuja, 1998). For twofold coordinated silicon center the singlet–triplet splitting ( $^1\text{S}_1 - ^3\text{T}_1$ ) large (~1.7 eV) witnessing of localized wave function.

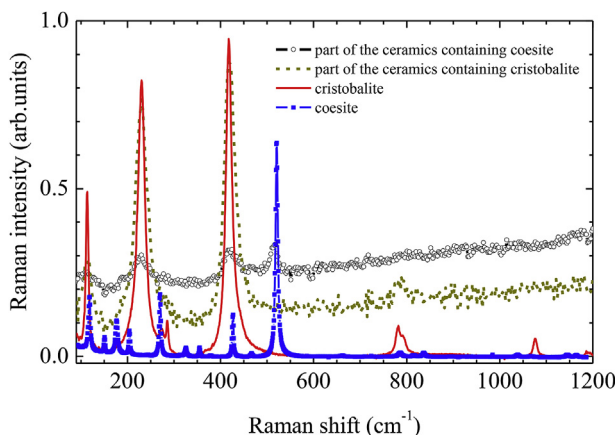
#### 3.1.2. ODC(I)

In silica glass with low level of oxygen deficiency the absorption band ( $^1\text{S}_1 \leftarrow ^1\text{S}_0$ ) is of negligible intensity (Trukhin and Fitting, 1999; Trukhin et al., 1979). However at 7.6 eV (Trukhin and Fitting, 1999; Trukhin et al., 1979), so called ODC(I) could be observed. The blue and UV bands appear due to photochemical transformation (Trukhin and Fitting, 1999):

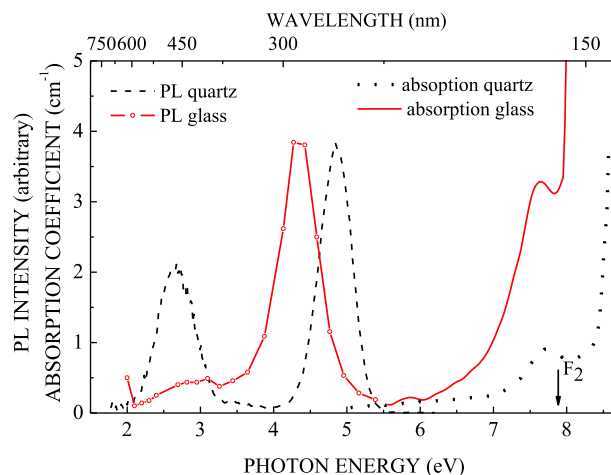


The measured decay of UV band is faster than of ODC(II) and is about 2 ns (Nishikawa et al., 1994; Boscaino et al., 1996). This acceleration was explained by influence of neighboring unknown defect (Trukhin and Fitting, 1999; Trukhin, 2011), showing on efficient deactivation processes of excited states competing the transition ( $^1\text{S}_1 \rightarrow ^1\text{S}_0$ ). The ODC(I) in silica explains the properties of localized states (Trukhin, 2011). In case of ODC(I) the blue band decay is strongly non-exponential and is observed in range of ms (Trukhin and Fitting, 1999). Triplet state is also sensitive to nearest unknown defect. The decay of such ODC(II) obtained by transformation of ODC(I) is strongly non-exponential (Trukhin and Fitting, 1999).

The ODC(I) in silica samples with high oxygen deficiency possesses high absorbance of corresponding band at about 100–200 cm<sup>−1</sup> (Trukhin and Fitting, 1999; Trukhin et al., 1979). Actually, the presented data in Fig. 2 are related to pure silica glass with low oxygen deficiency (KS-4V). The intensity of ODC(I) absorption there is about 3–4 cm<sup>−1</sup> and that of ODC(II) is much lower undetectable with our spectrophotometer. The UV band at 4.4 eV is more intense than the blue band in Fig. 2. Fast component of UV



**Fig. 1.** Raman spectra (532 nm cw laser excitation) of the ceramic sample in comparison with those of pure cristobalite from Kingma and Heymley (1994) and pure coesite from Gillet et al. (1990). Note the presence of background luminescence in the ceramics.



**Fig. 2.** Absorption spectrum ( $T = 290 \text{ K}$ ) and  $\text{F}_2$  laser excited ( $T = 80 \text{ K}$ ) time resolved (ns) PL of  $\gamma$ -ray irradiated  $\alpha$ -quartz and pure silica glass.

band of silica glass in case of excitation with F<sub>2</sub> laser is presented in Fig. 3. Determined value of time constant (about 2 ns) is in agreement with known data (Nishikawa et al., 1994; Boscaino et al., 1996). The blue band of silica glass is in the time range of about 200  $\mu$ s Fig. 4, which is much faster than 10 ms in case of ODC(II).

### 3.1.3. Luminescence of self-trapped exciton in silica glass

Another type of luminescence of silica glass is luminescence of self-trapped exciton exhibiting properties specific to disordered state (Trukhin, 1992; Trukhin et al., 2000), and its manifestation is not as descriptive as in  $\alpha$ -quartz crystal. The STE luminescence in silica glass demonstrates properties corresponding to strong influence of disordered state (Trukhin et al., 2000). The decay of STE luminescence is strongly non-exponential, Fig. 5. Thermal quenching of STE luminescence corresponds to non-monoenergetic value of thermal quenching energy with maximal density close to zero (Gee and Kastner, 1979), Fig. 5 insert. So, STE luminescence becomes intensive only at liquid helium temperatures. In that STE luminescence completely different from luminescence of ODC in silica, which is more less independent of temperature, at least for ODC(II). Because of that the energetic yield of STE luminescence in silica glass under ionizing radiation is much smaller ( $\sim 1\%$ ) with respect to that for crystalline  $\alpha$ -quartz ( $\sim 20\%$ ). In the case of photoexcitation it is possible to excite STE luminescence in silica in some pure samples and its temperature dependence well corresponds to that under x-ray excitation. However, the yield of photoluminescence is extremely small (less than 0.005 (Trukhin, 1992)). The spectrum of STE luminescence in silica is a broad band at 450–520 nm, Fig. 6.

## 3.2. $\alpha$ -quartz crystal

### 3.2.1. Luminescence of self-trapped exciton in $\alpha$ -quartz

Pure  $\alpha$ -quartz crystal possesses mainly luminescence of self-trapped exciton (STE) (Trukhin, 1992; Trukhin et al., 2000). STE provides luminescence band at 2.6 eV (Fig. 7) containing two-sub

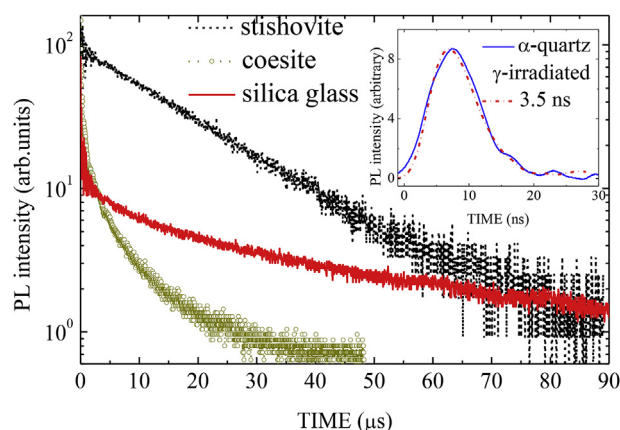


Fig. 4. Blue PL decay kinetics in SiO<sub>2</sub> polymorphous under F<sub>2</sub> laser, 80 K. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

bands with different thermal quenching and polarization parameters (Trukhin, 1992; Trukhin et al., 2000). Corresponding transitions are due to triplet-singlet and singlet-singlet states with small value of triplet-singlet splitting  $\sim 0.2$  eV witnessing of wavefunction spread in space (Trukhin, 2008). Under ionizing radiation, energetic yield of STE luminescence in  $\alpha$ -quartz crystal is high, about  $\sim 20(30)\%$  and therefore this luminescence is dominant in spectrum under such excitation even in not pure samples. The STE luminescence does not appear in pure recombination process such as thermally stimulated luminescence and afterglow for time bigger than 1 s. That also means lack of charge carriers self-trapping (Trukhin, 1992; Trukhin et al., 2000) Fig. 8.

Presence of impurities such as alkali ions, aluminum and germanium provides luminescence centers corresponding to these impurities (Trukhin and Truhins, 2012). STE luminescence and the impurities luminescence are very different from that of ODC-like.

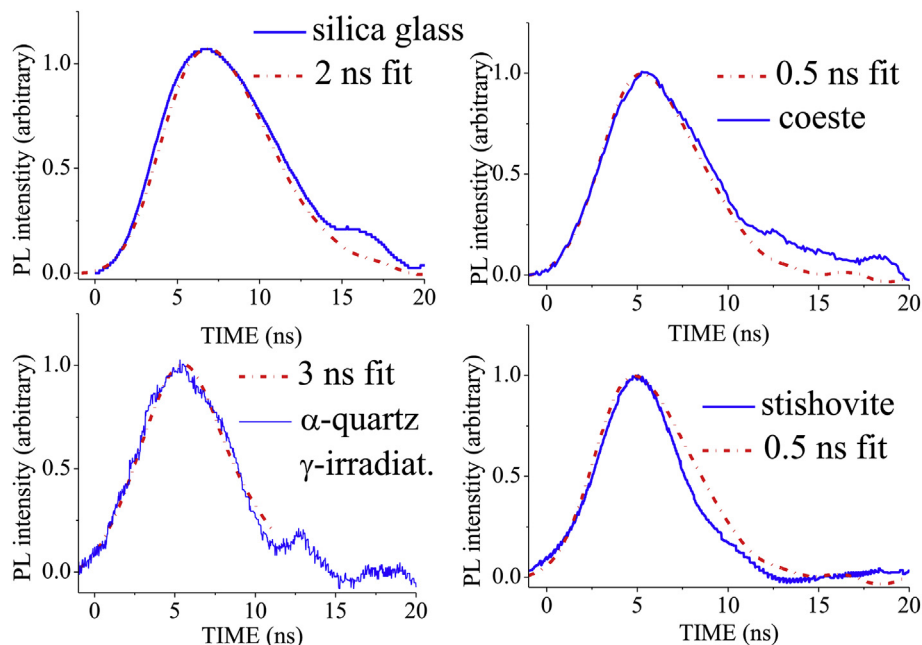
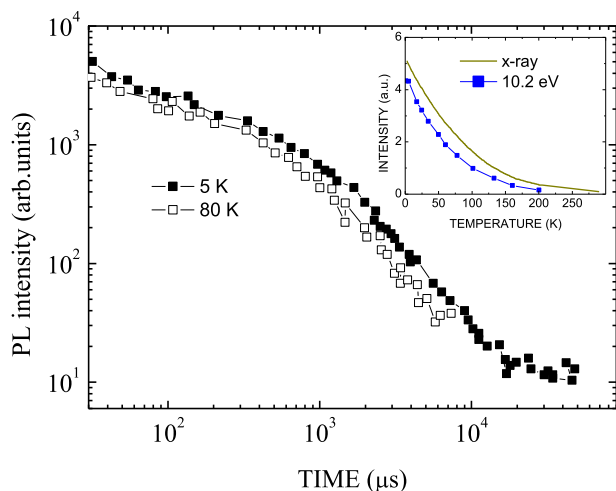
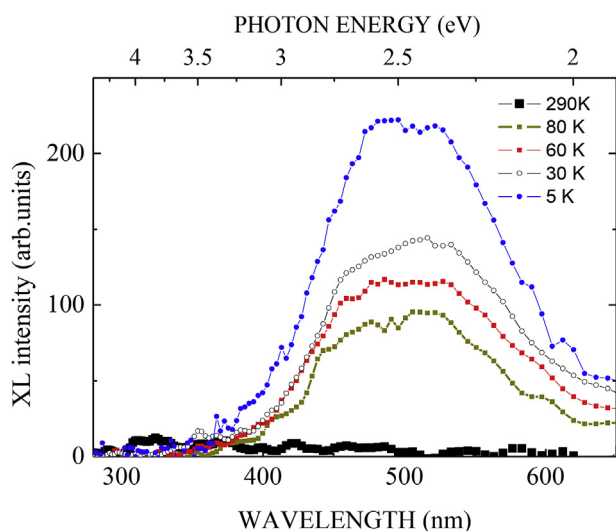


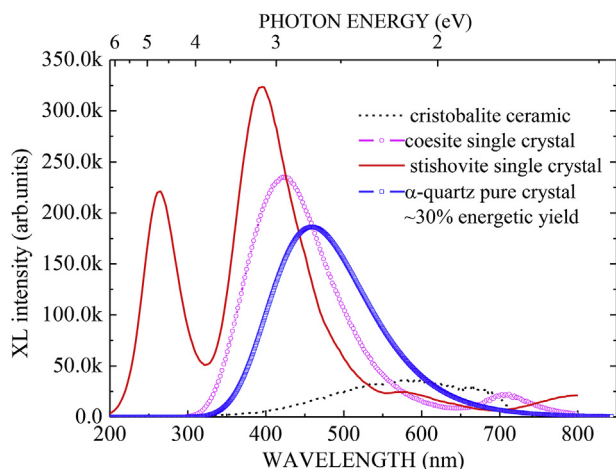
Fig. 3. UV PL decay kinetics in SiO<sub>2</sub> polymorphous under F<sub>2</sub> laser, 80 K. Limit of decay time constant determination is about 0.5 ns, then the curve labeled 0.5 ns corresponds to the shape of laser pulse.



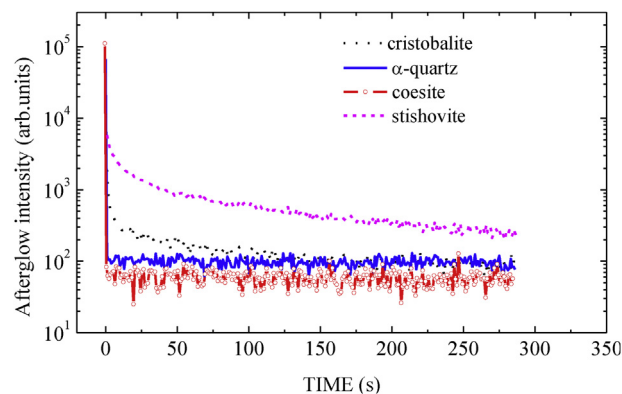
**Fig. 5.** Luminescence decay kinetics of pure silica glass under 10.2 eV pulses of spark in hydrogen atmosphere. Insert – thermal dependence of silica glass related luminescence intensity under x-ray and 10.2 eV photons.



**Fig. 6.** Silica glass x-ray excited spectra at different temperatures.



**Fig. 7.** X-ray excited luminescence spectra of polymorphous crystalline silicon dioxide crystals, comparison of energetic yields.



**Fig. 8.** Afterglow kinetics when x-ray is off at '0' time. Lack of afterglow in  $\alpha$ -quartz and coesite witnesses of STE. Afterglow in stishovite witnesses defect nature of the luminescence. Defects trap electron and holes, and then afterglow appears as following recombination. The signal of afterglow for  $\alpha$ -quartz and coesite is due to dark current of PM.

### 3.2.2. Radiation induced ODC-like defect in $\alpha$ -quartz

Irradiation of  $\alpha$ -quartz with neutron,  $\gamma$ -ray or dense electron beam provides luminescence similar to oxygen deficient silica glass, however it is not completely identical. Such luminescence seems at first was observed in neutron-irradiated quartz by Gee and Kastner (Gee and Kastner, 1979). Later, it was obtained also for the case of  $\gamma$ -irradiation (Cannas et al., 2004) Fig. 2. In both of these cases irradiation leads to creation of permanent luminescence centers at ambient temperatures. Irradiation of pure  $\alpha$ -quartz crystal with dense electron beam at low temperatures (checked at 10 K) leads to creation of analogous luminescence centers stable only at low temperatures (Trukhin et al., 2004). Heating of electron beam irradiated samples to 290 K removes induced centers. Spectral parameters of center induced in  $\alpha$ -quartz crystal are different from that of oxygen deficient silica glass. In case of electron beam and  $\gamma$ -irradiation the UV band is situated at 4.9 eV. Details can be found in (Cannas et al., 2004). The decay of UV band in irradiated  $\alpha$ -quartz under the excitation with F<sub>2</sub> laser is faster than that in the range of ODC(I), Fig. 3. The blue band in irradiated  $\alpha$ -quartz crystal is situated similarly to that of silica glass. However the decay of blue band is much faster in irradiated  $\alpha$ -quartz (~3 ns) than that of ODC(II) in silica glass (Cannas et al., 2004), Fig. 4 insert. In case of ODC(I) in silica glass there is wide spectrum of decay for blue band, Fig. 4. Fast decay of the blue band in  $\gamma$ -irradiated  $\alpha$ -quartz could be explained with creation only by ODC(I) type. In addition, it is found (Skuja et al., 1998) that  $\gamma$ -irradiated  $\alpha$ -quartz does not contain interstitial oxygen luminescence whereas neutron irradiated quartz possesses such luminescence. That is in contradiction with Si–Si model for ODC(I). Creation of oxygen vacancy by  $\gamma$ -irradiation in  $\alpha$ -quartz should be followed with luminescence of interstitial oxygen. There is no ODC(II) type defect in  $\gamma$ -irradiated  $\alpha$ -quartz. Surely, in  $\gamma$ -irradiated  $\alpha$ -quartz the luminescence under KrF laser was not detected, whereas in case of n-irradiated  $\alpha$ -quartz both types of defects are created (Gee and Kastner, 1979).

### 3.3. Cristobalite polycrystal

#### 3.3.1. Luminescence of cristobalite ceramic-like sample and manifestation of self-trapped exciton

Cristobalite is tetrahedron structured with density ~ 2.32–2.36 g/cm<sup>3</sup>. Cristobalite structure is tetragonal at temperatures below 250 °C and is cubic at high temperature. Si–O–Si angle is ~180°. There are hexagonal channels and cubic channels in different orientation of the cristobalite crystal.



However, the sample of cristobalite is polycrystalline, although no trace of silica glass, is observed in Raman spectrum Fig. 1. The energetic yield of the cristobalite luminescence was determined in comparison with STE luminescence of  $\alpha$ -quartz, Fig. 7. For the last yield is about 20% of absorbed energy of x-ray. We observed luminescence intensity of cristobalite to be approximately 4 times smaller than that of pure  $\alpha$ -quartz, therefore the energetic yield of our cristobalite sample is  $\sim 5\%$ . We checked if luminescence of cristobalite appears in afterglow Fig. 8, which is pure recombination process, and it was observed indeed. Then we made an experiment for determination of the afterglow spectral distribution. In Fig. 9 it is shown that afterglow takes place only in the band at 400 nm. The band at 600 nm practically does not participate in afterglow and correspondingly is not excited in recombination process. In Fig. 10, the afterglow curves for 430 nm and 600 nm bands after switching off x-ray are presented. We interpret the result for cristobalite as similar to that for  $\alpha$ -quartz, the band at 600 nm is STE of cristobalite without addition of defect related luminescence. We were able measure temperature dependence of luminescence intensity up to 20 K under x-ray excitation. That dependence the corresponding graph is presented in Fig. 11 for 600 nm luminescence intensity, decay time dependence on temperature under electron beam and x-ray excitations. There is sufficiently good correspondence in results under x-ray and electron beam excitations (last measurements only for  $T > 65$  K). Measured decay curves at different temperatures provide temperature sensitive component, the dependence is presented by time constant points. These points are determined with exponential approximation of luminescence decay at corresponding temperatures. Total decay under electron beam pulses is non-exponential. Therefore, the x-ray excited intensity dependence and the time constant thermal dependence is correspondent mutually. Then fundamental relation between yield of luminescence and corresponding time constant for the case of intra center transition is observed. In spite of complicated luminescence band composition as well as decay curves we were able extract 600 nm band and determine it decay time constant witnessing on intra center nature of electronic transition in conditions of excitation with ionizing radiation such as x-ray and electron beam. Thermal quenching energy of luminescence of cristobalite is 0.06 eV with frequency factor  $2 \cdot 10^6 \text{ s}^{-1}$ , Fig. 11. In addition a smaller energy ( $\sim 0.01$  eV) quenching process takes place with smaller frequency factor  $\sim 10^5 \text{ s}^{-1}$ .

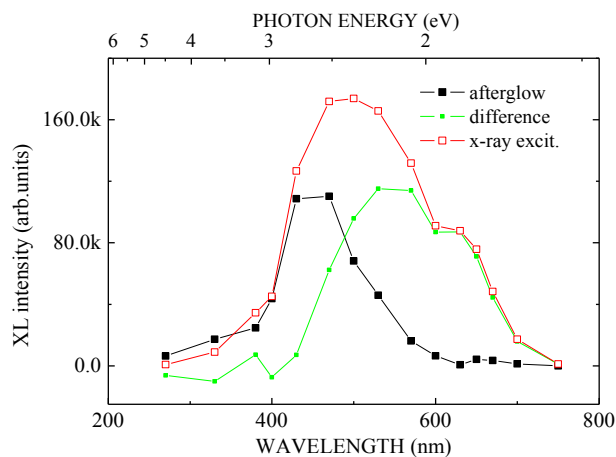


Fig. 9. Steady-state x-ray excited spectrum of cristobalite ceramic at 80 K (open squares) and afterglow spectrum after switching off x-ray. Small close circles – difference between steady-state and afterglow spectra.

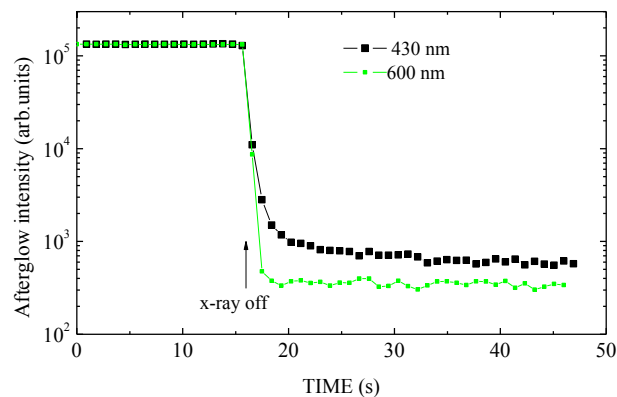


Fig. 10. Comparison of afterglow kinetics for x-ray excited cristobalite sample at 430 nm (close squares) and at 600 nm (small close circles). The intensities are normalized for period of steady-state x-ray excitation.

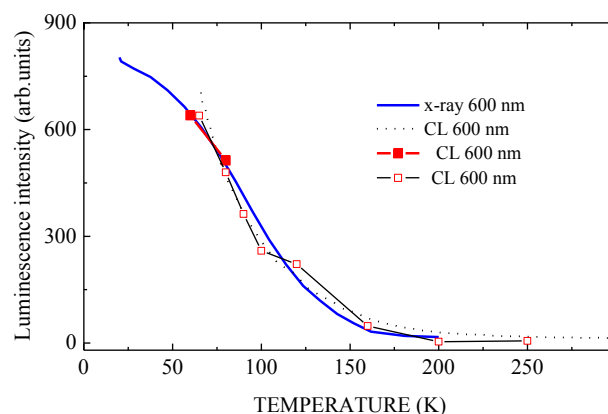


Fig. 11. Temperature dependence of cristobalite luminescence intensity under x-ray excitation (line) and under electron beam (dots). Temperature dependence of 600 nm luminescence decay time constant under electron beam pulses excitation are presented as well (close and open squares belonging to two measurements).

### 3.4. Rutile structured $\text{SiO}_2$ (stishovite)

Stishovite was synthesized by Stishov et al. (Stishov and Popova, 1961). Initially luminescence of stishovite was studied for the sample from Meteor Crater, Arizona (Fitting et al., 2001). Intensive blue band and long tail of lower intensity UV band was found. In synthetic stishovite single crystal both bands were also detected in x-ray excited luminescence Fig. 7 and photoluminescence (Trukhin et al., 2003, 2008, 2011; Truhins et al., 2004; Trukhin et al., 2014) with fast UV band Fig. 3 and slow blue band Fig. 4. The blue band possesses exponential decay at low temperature with time constant  $\sim 17 \mu\text{s}$ , Fig. 4. Blue band in stishovite does not contain fast component as opposed to coesite, Fig. 4. Effect of luminescence delayed was observed for stishovite. It is manifesting as intensity was growing sometime after end of excitation pulse for blue luminescence of stishovite (Trukhin et al., 2011). The effect was interpreted as delayed recombination luminescence associated with partial ionization of luminescence center during excitation and charge trapping on nearest traps. Water & OH group IR absorption bands. The use of graphite heater during crystal growth allows assume that those impurities could play role of traps (Trukhin et al., 2011). This effect of delayed luminescence was not observed in stishovite from Meteor Crater (Trukhin et al., 2011).

The duration of UV band is fast with characteristic time of  $\sim 2$  ns for excitation with ArF laser (193 nm) (Trukhin et al., 2014) and 0.5

ns for F<sub>2</sub> laser Fig. 3. Different time constant for UV luminescence shows excited luminescence center interaction with its surrounding. Indeed, partial acceleration under F<sub>2</sub> laser correlates with low quantum yield in respect to excitation with ArF laser. Nature for stishovite luminescence is assumed based on similarity with oxygen deficient silica and neutron -  $\gamma$ -irradiated  $\alpha$ -quartz. It is assumed creation in stishovite both ODC(II) and ODC(I) like defects during crystal growth. Both luminescence bands of stishovite could be excited in pure recombination process – afterglow for time longer than 1 s after x-ray was switched off and thermally stimulated luminescence Fig. 8. Therefore the defect responsible for luminescence is participating in charge carriers trapping followed by recombination. STE luminescence was not found in stishovite.

### 3.5. Coesite

Coesite was synthesized in laboratory (Coes, 1953). It was also found in Meteor Crater, Arizona. Intrinsic absorption threshold of coesite is situated at 8.5 eV for 290 K (Truhins et al., 2004).

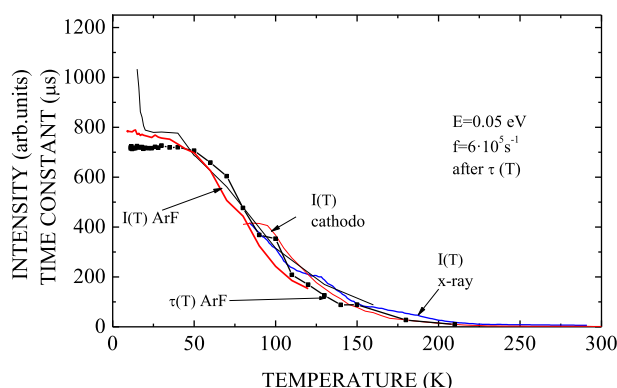
#### 3.5.1. Luminescence of self-trapped exciton in coesite

X-ray excitation of coesite single crystal induces luminescence band in the blue part of spectra with high energetic yield (~20%), Fig. 7 determined using as reference  $\alpha$ -quartz crystal as reference with the same small dimensions (~0.1 cm<sup>-3</sup>) as coesite sample. The key experiment is afterglow measurements for coesite crystal. That idea is based on previous data on behavior of STE in  $\alpha$ -quartz crystal, where the STE luminescence was not detected in pure recombination process such as afterglow and thermally stimulated luminescence Fig. 8. After x-ray excitation neither afterglow nor TSL were detected for coesite, which means that the luminescence could be STE like as in  $\alpha$ -quartz crystal.

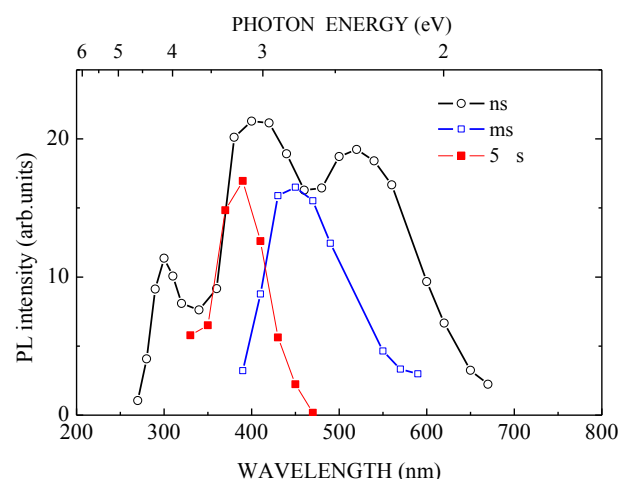
Correspondence between I(T) under x-ray and cathodoexcitation and ArF laser photoexcitation is essential for detection of time constant, Fig. 12. This could show that the temperature dependence of slow component is exactly the same as for x-ray and cathode luminescence intensity. If x-ray luminescence belongs to the STE, then slow component belongs to STE as well. The band at 460 nm, Fig. 13 corresponds to STE triplet-singlet transition. The fast ns component creating a blue band at 410 nm could be singlet-singlet transitions of STE, Fig. 13.

#### 3.5.2. ODC-like luminescence of coesite

Other luminescence bands of coesite could belong to a defect



**Fig. 12.** Comparison of x-ray excited and electron beam excited luminescence thermal dependences with that coesite excited with ArF laser (slow component) and slow component time constant thermal dependence. Good correspondence between these dependences witnesses that ionizing radiation induced luminescence of STE possesses slow decay.



**Fig. 13.** Time resolved PL spectra of coesite crystal under ArF laser pulses for different range of time. Close squares – ns range, close triangles – 5  $\mu$ s range, open circles – 0.7 ms range. T = 80 K.

centers. The spectrum for component in the range of 5  $\mu$ s is situated at 400 nm Fig. 13. The five  $\mu$ s time constant was determined after subtracting of exponent with slow decay. This component of decay weakly depends on temperature. Corresponding luminescence band in blue range of spectra could be ascribed to triplet-singlet transition of a defect center. The UV band at 300–280 nm with fast decay in ns range Fig. 13 could be ascribed to singlet-singlet transitions of that defect.

The decay of UV band is fast as in the case of stishovite and is equal to 0.5 ns independently of the temperature in the range 10–290 K Fig. 3. So, both bands of the defect in coesite weakly dependent on temperature and in that resemble ODC-like defect. The UV band is situated at 4.4 eV which is very similar to the case of silica glass. The quantum yield of UV luminescence is small as in the case of ODC(I). It is assumed that the existence of ODC(I) type defect also could be possible in coesite.

## 4. Discussion

### 4.1. Self-trapped exciton in silicon dioxide

Remarkable property of silicon dioxide  $\alpha$ -quartz is luminescence of self-trapped exciton (Trukhin, 1992; Trukhin et al., 2000). It has highest intensity under ionizing irradiation. In the Fig. 7 the spectra of x-ray excited luminescence are presented of the studied samples. The used  $\alpha$ -quartz crystal sample used in experiments was taken with dimensions similar to that of coesite and stishovite (~0.1 cm<sup>-3</sup>). Therefore, the energetic yield of x-ray excited luminescence was estimated for coesite and stishovite crystals. If energetic yield of  $\alpha$ -quartz was determined earlier as ~20% of absorbed excitation energy using as reference KJ-Tl crystal (see (Trukhin, 1992; Trukhin et al., 2000) and references therein), then both stishovite and coesite possess the same level of energetic yield because the luminescence intensities are of the same magnitude. The key experiment is related to the fact that STE luminescence of  $\alpha$ -quartz does not appear in pure recombination processes – afterglow and thermally stimulated luminescence (Trukhin, 1992; Trukhin et al., 2000). Switching off x-ray excitation leads to different behavior of  $\alpha$ -quartz and coesite as opposed to the stishovite crystal Fig. 8. The lack of afterglow Fig. 8 and high energetic yield under x-ray is a proof of STE existence in coesite.

Situation in cristobalite is similar but not equivalent. The band at

600 nm, Fig. 9 of cristobalite does not appear in afterglow, Fig. 10, and therefore could be assigned to STE. Let us discuss the convenience of proposed STE model for crystals with  $\alpha$ -quartz structure with respect to cristobalite. The proposed model for  $\alpha$ -quartz is Si–O bond rupture, created NBO relaxation and creation of a bond with bonding oxygen on opposite side of a channel, **c** or **x,y**. The NBO – BO bond energy is responsible for STE thermal stability. In the case of  $\alpha$ -quartz two channels provides two differently oriented STE with different luminescence polarization (Trukhin and Plaudis, 1979; Trukhin, 1992; Tanimura and Halliburton, 1986). Energy of cristobalite STE thermal quenching is 0.06 eV with frequency factor  $2 \cdot 10^6 \text{ s}^{-1}$ , Fig. 11. From dependence shown in Fig. 11 a smaller value of quenching could be obtained with activation energy 0.016 eV and  $\sim 10^4 \text{ s}^{-1}$  frequency factor. Presumably that could correspond to other STE. The STE thermal quenching energy is lower than that for  $\alpha$ -quartz. It seems that the Si–O bond rupture could still be a good model for STE also in cristobalite. For NBO – BO bond creation there are hexagonal and cubic channels. So, two values of thermal quenching energy observed may be explained with NBO – BO bond creation in those two channels. Future studies of a single crystal could resolve possible STE model in cristobalite.

#### 4.2. Luminescence of host material defects of silicon dioxide

Let us analyze host defect luminescence of silicon dioxide. The case of stishovite is an example of silicon dioxide where only defect luminescence is observed. It could be excited by photons with energy below intrinsic absorption threshold (8.75 eV (Truhins et al., 2004; Trukhin et al., 2008)). Both bands of stishovite luminescence participate in recombination processes therefore could not be attributed to STE of silicon dioxide. High energetic yield of the stishovite luminescence proves that the defect is host material. In silicon dioxide materials – oxygen deficient silica glass, neutron-  $\gamma$ -irradiated  $\alpha$ -quartz as well as grown single crystals of stishovite and coesite the luminescence with two bands blue and UV are observed. Pure oxygen deficient silica glass possesses such luminescence, corresponding luminescence center could be unequivocally ascribed to similar host material defect in others materials as well. Similarities of luminescence properties with silica glass allow to assume that corresponding defect could exist in irradiated  $\alpha$ -quartz as well as in as grown stishovite and coesite. The fact that this luminescence was not observed in non-irradiated  $\alpha$ -quartz could show that defect could not exist in undamaged chain of tetrahedral network. In un-damaged network of crystal and even continuous network of glass the self-trapped exciton is manifested. Existence of such defect in tetrahedron structured as grown coesite demonstrates that the high pressure conditions stimulate such defect as well as provide possibility for STE existence. Essentially that was observed on example of stishovite grown at much higher pressure. So, in some way that could explain properties of silica glass, which structure could be imagined as density fluctuation. Therefore stishovite-like structural motifs with higher density could be responsible for mentioned ODC(II) and ODC(I) defect. This dense motif of occupied volume is compensated with free volume. Conditions of high pressure for dense modifications of silicon dioxide stimulate situation favorable for center existence in dense octahedron structured stishovite and even in tetrahedron structured coesite. In coesite structure provides situation similar to silica glass where ODC coexists with self-trapped exciton.

#### 5. Conclusions

In four silicon dioxide materials – oxygen deficient silica glass, neutron-  $\gamma$ -irradiated  $\alpha$ -quartz as well as grown single crystals of stishovite and coesite the luminescence with two bands – blue and

UV were observed. Luminescence center could ascribe to host material defect. Corresponding defect could exist in irradiated  $\alpha$ -quartz, stishovite and coesite similar to defect of oxygen deficient silica glass. Discovery of luminescence center in stishovite and coesite is basis for hypothesis of existence of corresponding structural motifs existence in silica glass and irradiated  $\alpha$ -quartz. Nature of defect related luminescence of cristobalite is not clear up to now.

As received  $\alpha$ -quartz, pure silica glass, as grown coesite crystal and cristobalite, contains  $\text{SiO}_4$  tetrahedron as main element of structure and exhibit self-trapped exciton luminescence. No STE was observed in stishovite. Stishovite contains  $\text{SiO}_6$  octahedron as main element of structure, exhibits only defect related luminescence.

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