

Luminescence of silicon dioxide different polymorph modification: Silica glass, α -quartz, stishovite, coesite

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Luminescence of Silicon Dioxide Different Polymorph Modification: Silica Glass, α -Quartz, Stishovite, Coesite

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Abstract. Stishovite, coesite, oxygen deficient silica glass as well as irradiated α -quartz, exhibit two luminescence bands: a blue one and an UV one both excitable in the range within optical gap. There are similarities in spectral position and in luminescence decay kinetics among centers in these materials. The interpretation was done on the model of Oxygen Deficient Centers (ODC) [1]. The ODC(II) or twofold coordinated silicon and ODC(I) are distinguished. ODC(I) is object of controversial interpretation. The Si-Si oxygen vacancy [2] and complex defect including latent twofold coordinated silicon [3] are proposed. Remarkably, this luminescence center does not exist in as grown crystalline α -quartz. However, destructive irradiation of α -quartz crystals with fast neutrons, γ rays, or dense electron beams [4-6] creates ODC(I) like defect. In tetrahedron structured coesite the self trapped exciton (STE) luminescence observed with high energetic yield ($\sim 30\%$) like in α -quartz crystals. STE in coesite coexists with oxygen deficient-like center. In octahedron structured stishovite STE was not found and only ODC exists.

INTRODUCTION

Silicon dioxide exists in many polymorph modifications including glassy state. This situation provides opportunity investigate properties of host defect and electronic excitation of silicon dioxide through comparison of properties between these modifications. Silicon dioxide is wide gap insulator for which luminescence brings information about defect and electronic excitations. Previously defect luminescence of silicon dioxide was studied in [1-8]. Luminescence related to electronic excitations also was studied (see e.g. [8-10]). For widely studied crystalline silicon dioxide – α -quartz, purest samples manifest mainly luminescence of self-trapped excitons [8-10]. Silica glass is also sufficiently well studied. Remarkable for silica glass is luminescence of defects and localized states [1-8]. Luminescence of self-trapped exciton in silica glass is also observed [10], however it is not so efficient as in α -quartz crystal. On this base a possibility for understanding of fundamental properties of other modifications such as stishovite and coesite appears. Different crystalline modification of silicon dioxide - as grown stishovite and coesite, oxygen deficient silica glass as well as irradiated α -quartz, exhibit two luminescence bands: a blue one and an UV one both excitable in the range within optical gap. For coesite also luminescence excitable only in intrinsic absorption takes place [11] and it was ascribed to self-trapped exciton. For stishovite only luminescence of defect was observed [11].

CHARACTERIZATION OF THE MATERIALS

Silicon dioxide could exist in many polymorph modifications. The sp^3 hybridization provides a family of tetrahedron structured materials. These are α -quartz ($\sim 2.65 \text{ g/cm}^3$), silica glass ($\sim 2.5 \text{ g/cm}^3$) and coesite ($\sim 3 \text{ g/cm}^3$).

Stishovite ($\sim 4.3 \text{ g/cm}^3$) based on another manner of silicon hybridization – d^2sp^3 , providing octahedral surrounding of silicon with oxygen ions.

EXPERIMENTAL

The sample of investigation were high purity α -quartz, pure silica glass of KS-4V type with different level of oxygen deficiency, synthetic stishovite single crystal and synthetic coesite single crystal. Single crystals of stishovite have been 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 [7]. The α -quartz crystal sample was cut for dimension corresponding to that of stishovite and coesite $0.2\text{--}0.4\text{--}0.6\text{--}0.9\text{ mm}^3$ therefore energetic yield for coesite and stishovite luminescence could be estimated.

The KrF, ArF and F_2 laser (model PSX-100, made by Neweks, Estonia), x-ray tube and pulsed electron beam equipment with electron energies 6 KeV and 0.2–1 μs pulse duration were luminescence excitation source. The x-ray tube was with W anticathode working in regime 50 kV 20 mA. The measurements were realized with the use of helium refrigerator. Luminescence detection was realized with a photomultiplier tube H6780-04. An oscilloscope (Textronic TDS 2022B) was exploited for decay curve registration. The X-ray excited spectra were measured in the photon counting regime with use of with Hamamatsu H8259-02 module.

X-RAY EXCITED LUMINESCENCE IN α -QUARTZ, STISHOVITE AND COESITE CRYSTALS

Remarkable property of silicon dioxide α -quartz is luminescence of self-trapped exciton [8–10]. It is most bright under ionizing irradiation. In the Fig.1 the spectra of x-ray excited luminescence spectra of the studied samples are presented. the energetic yield of x-ray excited luminescence was estimated for coesite and stishovite

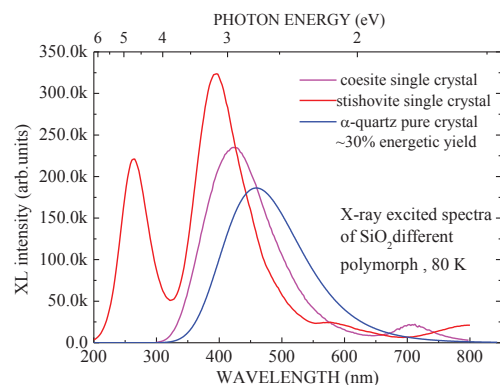


FIGURE 1. X-ray excited luminescence spectra of crystalline silicon dioxide crystals. Comparison or energetic yield.

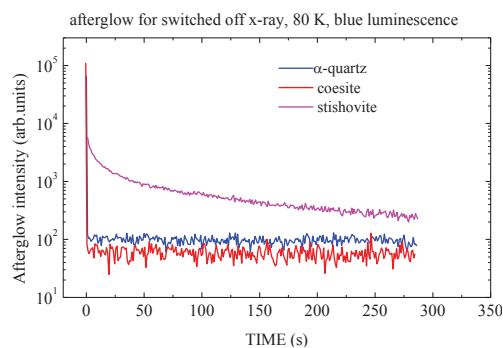


FIGURE 2. Afterglow kinetics when x-ray is off at '0' time. The signal of afterglow for α -quartz and coesite is due to dark current of PM.

crystals by comparison with that of α -quartz ($\sim 30\%$ of absorbed excitation energy [10]). Correspondingly Fig.1 stishovite and coesite samples possess the same level of energetic yield. The key experiment is related to the fact that STE luminescence of α -quartz does not appear in pure recombination processes – afterglow and thermally stimulated luminescence [8–10]. Switching off x-ray excitation leads to different behavior of α -quartz and coesite from one hand and the stishovite crystal from the other, Fig.2. So the lack of afterglow in coesite, Fig.2 and high energetic yield of coesite luminescence under x-ray is a prove of STE existence in coesite. Contrary in stishovite both luminescence bands at 400 nm and 260 nm participate in afterglow (in Fig.2 the data shown for blue band) as well as in thermally stimulated luminescence [11] and therefore both bands belong to a defect. Evidently that high energetic yield of the stishovite luminescence witness that the defect is host material.

SILICA GLASS

ODC(II) or twofold coordinated silicon

In silica glass with high level of oxygen deficiency [1] 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 (F₂ laser).

In the range of 5 eV the ODC(II) or the twofold coordinated silicon center is excited through singlet-singlet transitions ($^1S_1 \leftarrow ^1S_0$) [1]. Emission of UV band at 4.4 eV ($^1S_1 \Rightarrow ^1S_0$) is with time constant about 4.5 ns [12]. The blue emission at 2.7 eV is due to triplet-singlet ($^3T_1 \Rightarrow ^1S_0$) transitions (exponential decay, rare for glasses) with time constant about 10 ms [1, 12]. Population of the triplet state is due to $^1S_1 \Rightarrow ^3T_2 \Rightarrow ^3T_1$ [12]. The UV bands time constant is little changed only from 4.6 ns to 4.1 ns [13.14] with temperature in spite of the transition $^1S_1 \Rightarrow ^3T_2$ is thermally activated [12]. For twofold coordinated silicon center the singlet-triplet splitting ($^1S_1 - ^3T_1$) large (~1.7 eV) witnessing on localized wave function.

ODC(I)

In silica glass with low level of oxygen deficiency the absorption band ($^1S_1 \leftarrow ^1S_0$) is of negligible intensity [3.15]. However at 7.6 eV [3.15], so call ODC(I) could be observed. The blue and UV bands appear due to photochemical transformation:



The measured decay of UV band is faster than for ODC(II) and is about 2 ns [13.14]. Acceleration was explained by influence of nearest unknown defect [3, 6, 16], showing on efficient processes of deactivation of excited states, competing the transition ($^1S_1 \Rightarrow ^1S_0$). The ODC(I) in silica is base for properties of localized states [17]. The blue band in the case of ODC(I) decay strongly non-exponential, however in the range of ms [3] - triplet state is sensitive to nearest unknown defect.

The ODC(I) in silica samples with high oxygen deficiency possesses intensity of corresponding absorption band about 100 – 200 cm⁻¹ [3, 15]. Actually, the presented data Fig.3 are related to pure silica glass with low oxygen deficiency (KS-4V).

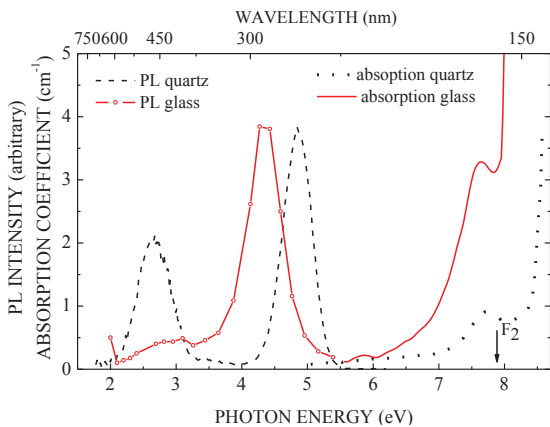


FIGURE 3. Absorption spectrum (T=290 K) and F₂ laser excited (T=80 K) time resolved (ns) PL of γ -ray irradiated a-quartz and pure silica glass.

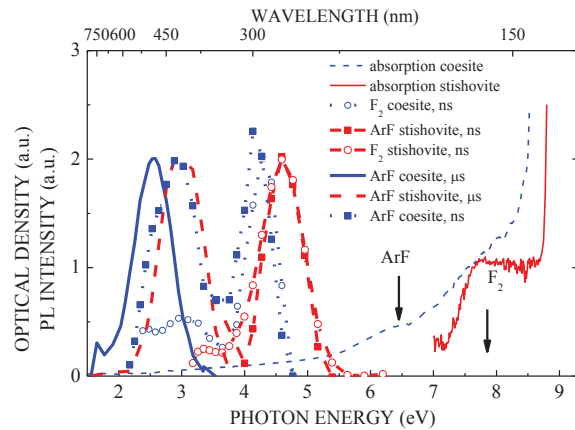


FIGURE 4. Optical absorption and time resolved PL spectra of stishovite and coesite crystals under ArF and F₂ lasers, 80 K.

The intensity of ODC(I) absorption is about 3-4 cm⁻¹ and that of ODC(II) is much lower even not detected with our spectrophotometer. The UV band at 4.4 eV prevails the blue band Fig.3. Fast component of UV band of silica glass excited with F₂ laser possesses time constant is about 2 ns in agreement with known data [13.14]. The blue band of silica glass is in the time range about 200 μ s, which is much faster than 10 ms of the case of ODC(II).

Luminescence of self-trapped exciton in silica glass

Another luminescence of silica glass is luminescence of self-trapped exciton exhibiting specific to disordered state properties [10], and its manifestation is not as effective as in α -quartz crystal. The energetic yield of STE luminescence in silica glass under ionizing radiation is much smaller ($\sim 1\%$) with respect to that for crystalline α -quartz ($\sim 30\%$). The STE luminescence in silica glass exhibits properties corresponding to influence of disordered state [8,10]. The decay of STE luminescence is non-exponential. Thermal quenching of STE luminescence corresponds to non-monoenergetic value of thermal quenching energy with maximal density close to zero [8,10]. So, STE luminescence becomes intensive only at liquid helium temperatures. In that STE luminescence is completely different from luminescence of ODC in silica, which is more or less independent on temperature, at least for ODC(II).

α -QUARTZ CRYSTAL

Luminescence of self-trapped exciton in α -quartz

Pure α -quartz crystal possesses mainly luminescence of self-trapped exciton (STE) [8,10]. STE provides luminescence band at 2.6 eV (Fig.1) containing two sub bands with different thermal quenching and polarization parameters [8,10]. Corresponding transitions are due to triplet-singlet and singlet-singlet states with small value of triplet-singlet splitting ~ 0.2 eV witnessing of wavefunction spread in space [17]. Under ionizing radiation energetic yield of STE luminescence in α -quartz crystal is high, about $\sim 30\%$ 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 [8,10] Fig.2.

Presence of impurities such as alkali ions, aluminum, germanium provides luminescence centers corresponding to these impurities [9]. STE luminescence and the impurities luminescence are very different from that of ODC-like.

Radiation induced ODC-like defect in α -quartz

Irradiation of α -quartz with neutron, γ -ray or dense electron beam provides luminescence similar to oxygen deficient silica glass, however not identical. Such luminescence was observed in n-irradiated quartz [4]. After, it was obtained also for the case of γ -irradiation [6] Fig.3. In both cases irradiation leads to creation of permanent luminescence centers at ambient temperatures. Later [5], irradiation of pure α -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. Heating of samples to 290 K removes induced centers. Spectral parameters of center induced in α -quartz crystal are different from that of oxygen deficient silica glass. The UV band is situated at 4.9 eV for the case of electron beam and γ -irradiation. Details could be found in [6]. The decay of UV band in irradiated α -quartz is fast under excitation of F_2 laser, that in the range of ODC(I). The blue band in irradiated α -quartz crystal is situated similarly to that of silica glass. However the decay of blue band is much faster in irradiated α -quartz (~ 3 ns) than that for ODC(II) in silica glass [6]. Fast decay of the blue band in irradiated α -quartz could be explained with creation by γ -irradiation only ODC(I) type. Also it is found [18] that γ -irradiated α -quartz does not contain oxygen luminescence whereas neutron irradiated quartz possesses such luminescence. That is in contradiction with Si-Si model of ODC(I). Creation of oxygen vacancy by γ -irradiation of α -quartz should be followed with luminescence of interstitial oxygen.

There is no ODC(II) type defect in γ -irradiated α -quartz. Under KrF laser in γ -irradiated α -quartz was not detected luminescence. Whereas in the case of n-irradiated α -quartz both type of defect are created [4].

RUTILE STRUCTURED SiO_2 (STISHOVITE)

Stishovite was synthesized by Stishov et al. [19]. Initially luminescence of stishovite was studied for the sample from Meteor Crater, Arizona [20]. Intensive blue band and long tail of lower intensity UV band was found. Later,

for synthetic stishovite single crystal both bands also detected in x-ray (Fig.1) and photoluminescence [11, 21-24] with fast UV band(~ 2 ns) and slow blue band (17 μ s) Fig.4. Effect of delayed luminescence was observed as period of intensity growth long time after end of excitation pulse for blue luminescence of stishovite [25]. The effect was interpreted as recombination type of delayed luminescence connected with partial ionization of luminescence center during excitation and charge trapping on nearest traps. water & OH group and carbon impurity could play role of traps [21-24].

The duration of UV band is fast with characteristic time ~ 2 ns for excitation with ArF laser (193 nm) [23] and 0.5 ns for F_2 laser. Different time constant for UV luminescence shows on excited luminescence center interaction with surrounding. Nature for stishovite luminescence is assumed on a base of similarity with oxygen deficient silica and neutron - γ -irradiated α -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 switch off x-ray and thermally stimulated luminescence Figs.1,2. Therefore the defect responsible for luminescence is participating in charge carriers trapping and followed recombination.

COESITE

Coesite was synthesized in laboratory [25]. It also was found in Meteor Crater, Arizona. Intrinsic absorption threshold of coesite is situated at 8.5 eV for 290 K Fig.4 [11].

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 ($\sim 30\%$, Fig.1). After x-ray excitation neither afterglow nor TSL were detected for coesite. Then the x-ray excited luminescence could be STE like as in α -quartz crystal.

Essential is correspondence between $I(T)$ under x-ray and cathodoexcitation, from one hand and focused ArF laser beam photoexcitation allowing detection of time constant, Fig. 5. This shows that slow component temperature

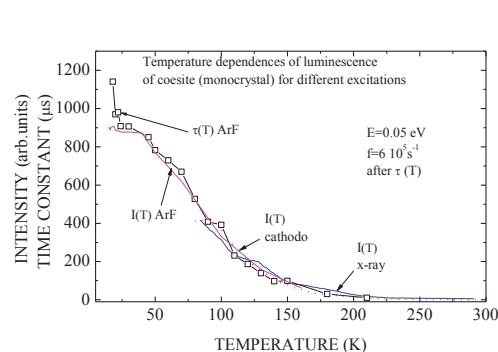


FIGURE 5. Comparison of x-ray excited and electron beam excited luminescence thermal dependences with that excited with ArF laser (slow component) and slow component time constant thermal dependence. Good correspondence between these dependences witnesses that ionizing radiation induced luminescence of STE possesses slow decay.

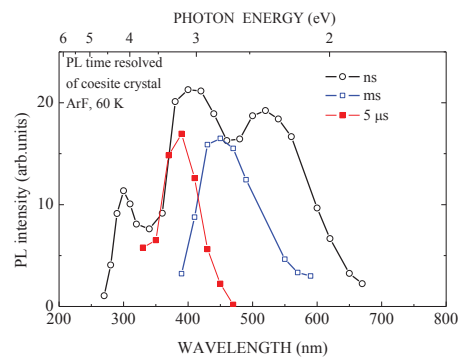


FIGURE 6. Time resolved photoluminescence spectra of coesite crystal under ArF laser pulses. the band of component with time constant \sim ms belong to triplet-singlet transition but the band ~ 410 nm with fast decay belongs to singlet-singlet transitions of the self-trapped exciton. The band at 390 nm with time constant ~ 5 μ s belongs to triplet-singlet transitions and the band at 300 nm with fast decay belongs to singlet-singlet transition of the ODC(I)-like defect. The band at 550 nm does not yet get interpretation.

dependence is exactly the same as for x-ray and cathode luminescence intensity. X-ray luminescence belongs to the STE, then slow component belongs to STE as well. Increase of decay time constant below 20 K could correspond to STE triplet state splitting in zero magnetic fields. The band at 460 nm, Fig.6 (ms) 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.6.

ODC-like luminescence of coesite

The UV band at 300 nm and at 570 nm band of ns range as well as band at 400 nm with time constant 5 μ s of Fig.6 could correspond to defect luminescence. The last band in blue range of spectra could be ascribed to triplet-singlet transition of a defect center. This band can be excited with KrF laser (248 nm). The UV band 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 in the range 10 – 290 K. So, both bands of the defect in coesite weakly dependent on temperature and in that resemble ODC-like defect. The UV band Figs. 4, 6 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 assume existence of ODC(I) type defect also in coesite.

DISCUSSION

In silicon dioxide materials – oxygen deficient silica glass, neutron- γ -irradiated α -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 suppose that corresponding defect could exist in irradiated α -quartz as well as in as grown stishovite and coesite. The fact that this luminescence was not observed in non-irradiated α -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 demonstrate that conditions of high pressure stimulate such defect from one hand and provide situation for STE existent from other. Essentially that is seen 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 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. So in array from crystalline α -quartz to coesite and stishovite conditions for creation of ODC like defect are ameliorating. So, silica glass joints all manifestations of structural elements in one material because of disordered state.

CONCLUSIONS

In four silicon dioxide materials – oxygen deficient silica glass, neutron- γ -irradiated α -quartz as well as grown single crystals of stishovite and coesite the luminescence with two bands blue and UV are observed. Luminescence center could ascribe to host material defect. Corresponding defect could exist in irradiated α -quartz, stishovite and coesite similar to defect of oxygen deficient silica glass. Discovery of luminescence center in stishovite and coesite is base for hypothesis of corresponding structural motifs existence in silica glass and irradiated α -quartz. As received α -quartz, pure silica glass and as grown coesite crystal exhibit self trapped exciton luminescence. No STE was observed in stishovite.

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