

Luminescence of α -quartz crystal and silica glass under excitation of excimer MARK lasers

ArF (193 nm), KrF (248 nm)

A.N. Trukhin

Institute of Solid State Physics, University of Latvia, LV-1063, Riga, Latvia

ABSTRACT

Luminescence of crystalline α -quartz and silica glass was studied under focused laser excitation. It was found that in crystalline α -quartz the luminescence of self-trapped exciton (STE) is excited in two-photon regime with ArF (193 nm) excimer laser. In the case of KrF (248 nm) laser excitation mainly luminescence related to near surface area is seen even without laser beam focusing. The near surface luminescence has an emission band similar to that of STE in bulk. Temperature quenching is also similar, therefore this luminescence is attributed to STE created in the area of surface. Luminescence decay kinetic of surface STE is longer than bulk STE decay (tens of ms compared to 1 ms at 80 K). Electron or/and hole self-trapping near the surface is assumed. Their recombination could provide longer duration of surface STE luminescence. Similar surface luminescence was not excited with ArF (193 nm) excimer laser. The nature of absorption for laser 248 nm photons at surface is not yet clear.

Luminescence of silica glass of III type excited with focused beam of KrF (248 nm) laser resembles that of previously studied luminescence of STE in silica.

1. Introduction

Luminescence of silicon dioxide high purity samples of α -quartz crystal is mainly connected with emission of self-trapped exciton (STE). Though the corresponding luminescence was discovered in the 60-ties [1], it was unambiguously assigned to a self-trapped exciton only in the end of 70-ties [2–4]. Absence of STE luminescence in pure recombination process is a key property. It agrees with absence of electron and hole self-trapping in α -quartz crystal [5,6].

For silica glass luminescence was excited with x-ray irradiation [1] only in pure silica glass containing OH groups, similarly to quartz crystal. Silica glass, obtained by fusion of impure quartz, possesses luminescence mainly attributable to impurities and host material defects [7]. Essential contribution to understanding of the nature of STE luminescence in silica glass was brought by observation of transient absorption [2]. This effect is similar to that observed in quartz crystal. The absorption bands were attributed to E'-center and non-bridging oxygen. Corresponding bands are situated at about 5.6 eV and 4.7 eV. Luminescence decay of silica glass is non-exponential [8] contrary to exponential decay of quartz crystal [9]. The STE luminescence of silica glass should be searched in pure sample with little influence of defects. For this purpose mainly silica glass of type III is appropriate because even very pure silica glass of type IV possesses luminescence of localized states [10], where luminescence is mainly due to oxygen

deficient centers (ODC). Number of such centers is strongly reduced by the presence of OH groups in silica type III [11]. Authors of [9] reported on STE detection in silica glass by photoexcitation. The yield of photoluminescence they observed was very small, about 0.001. The STE in silica glass does not participate in recombination processes though a self-trapped hole (STH) was discovered for this material [12]. The STH in silica glass participates in processes related to the localized states [13].

In the case of quartz crystal the yield of photoluminescence is about 0.05 [9], i.e., also too small for excitation in the range of exciton absorption bands 9–11 eV [9] (limitation of energy is caused by use of LiF window for experiments at low temperatures). From other hand, the energetic yield of x-ray excited STE luminescence is about 25% of absorbed excitation energy in the case of quartz crystal and about 1% in the case of silica glass [9]. So, there is an evident discrepancy between high energy yield for excitation with x-rays and low quantum yield for photoexcitation. In the case of quartz crystal the problem was studied by implementing measurements with the use of ArF laser (193 nm, 6.4 eV) for two-photon excitation of STE luminescence. Laser light excites STE luminescence in the bulk as in the case of x-ray excitation and not in the near surface area as in the case of photoexcitation with VUV photons [14]. The efficiency of the two-photon STE excitation was estimated with respect to sodium salicylate one-photon excited luminescence and it was found that intensities in both cases are of the same

order of magnitude in the same geometry of detection. High efficiency of STE luminescence in α -quartz under two-photon excitation allows support the idea of modified structure of near surface area of polished sample determining the low yield of one-photon excited luminescence. Unfortunately the use of ArF (193 nm) laser for STE luminescence in silica glass was not successful because of strong luminescence of this material in one-photon regime (see e.g. [10]) under such excitation. In the present paper we tried to excite STE luminescence in silica glass type III with the use of KrF (248 nm) laser and compare the results with quartz crystal. It is assumed that in such situation one-photon excited defect-related luminescence will affect the STE luminescence to a smaller extent.

2. Experimental procedure

The samples under investigation were nominally pure α -quartz crystals and silica glass of III type (KY-1). Presence of OH groups in silica type III strongly diminishes concentration of oxygen deficient centers (ODC) [11]. Before measurements the samples were polished and annealed at 500 °C.

Photon counting mode was instrumented with Hamamatsu H8259-02 module. For current mode a photomultiplier tube H6780-04 was used. Luminescence decay curves were recorded by the Tektronics TDS 2022B oscilloscope, each curve being averaged over 128 pulses. Time-resolved luminescence spectra were extracted by integration of decay curves measured at each specific wavelength. The ArF (193 nm wavelength) and KrF (248 nm wavelength) excimer lasers, model PSX-100 of Neweks (Estonia) with pulse energy of up to 5 mJ and pulse duration of 5 ns, were used to excite luminescence. Two photon of KrF (10 eV) corresponds to exciton absorption band at 10.5 eV in quartz.

Luminescence emission was registered in a direction perpendicular to the excitation laser beam. The samples were carefully cleaned and mounted on a holder, no glue was used. Measurements were performed at 10–350 K sample temperatures.

Luminescence was detected with the help of a grating monochromator (MCD-1) with slit width of about 1 mm corresponding to 1.5 nm spectral resolution. Luminescence measurement details are described in [9,10,13]. The measured curves are presented in the figures as recorded, therefore they reflect the level of errors.

3. Results

3.1. α -quartz crystal

In the Fig. 1 photoluminescence decay curves for the blue luminescence of quartz crystal are presented. Detection was done with H8259-02 photon counting module suitable for the slow luminescence (slower

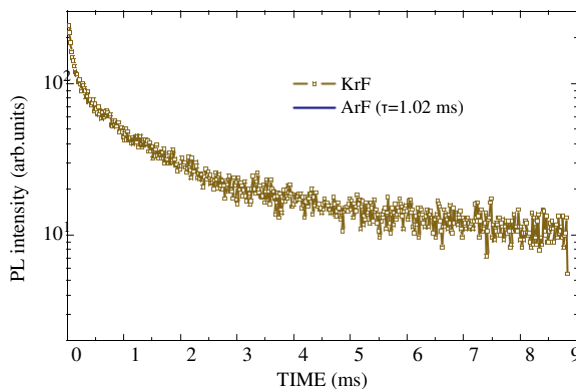


Fig. 1. Decay kinetics of photoluminescence at 440 nm excited with focused beam of ArF (193 nm) and KrF (248 nm) lasers in pure α -quartz sample at 80 K.

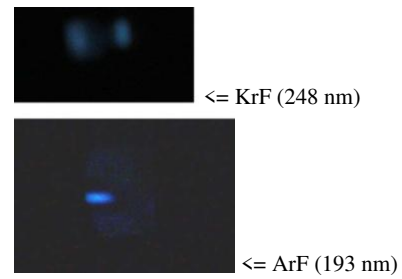


Fig. 2. Photographic image of thick quartz sample excited with KrF (248 nm) (the image is not well focused). Luminescing parts belong to two surfaces of the sample. Absence of light between them means that only surface is luminescent. Picture in the case of ArF (193 nm) laser excitation is presented for comparison. In both cases the excitation beams are focused in the middle of bulk of sample.

than tens of μ s). The excitation was done by ArF (193 nm) and KrF (248 nm) lasers through long focus lens. Remarkable difference is seen for two kinds of excitation. The case of ArF (193 nm) laser completely corresponds to the previously published [14] curve detected in the current mode of photomultiplier. In the two photon excitation regime the STE luminescence of quartz with decay about 1 ms is detected. However, irradiation with KrF (248 nm) laser provides different decay curve.

In Fig. 2 the photo of quartz crystal sample luminescence is presented for the case of KrF (248 nm) and ArF (193 nm) lasers excitation. It can be seen that only light from two surfaces of a thick sample appear under KrF (248 nm) laser with focusing in the middle of bulk. The ArF (193 nm) laser causes emission in the bulk of sample (labeled as STE excited with ArF, Fig. 2). Excitation with KrF (248 nm) laser without beam focusing also provides luminescence of surfaces, though less intensive.

In Fig. 3 the luminescence spectra of quartz crystal under x-ray, ArF (193 nm) and KrF (248 nm) excitation are presented. Surprisingly, there is no remarkable difference in spectra corresponding to those excitation cases. Note, x-ray excited luminescence spectrum of pure quartz crystal sample is STE luminescence [9].

In Fig. 4 the temperature dependences of the studied sample of quartz crystal excited with pulses of ArF (193 nm) laser are presented. As previously [9,14], we observe two stages of temperature quenching for cases of time resolved intensity (intensity was determined as integral under decay curve for corresponding temperature) and time constant. First stage begins at about 130 K and the second begins at about 180 K. Luminescence quenches at 200 K. At low temperature (at about 10 K) the observed peculiarities in decay (appearance of very

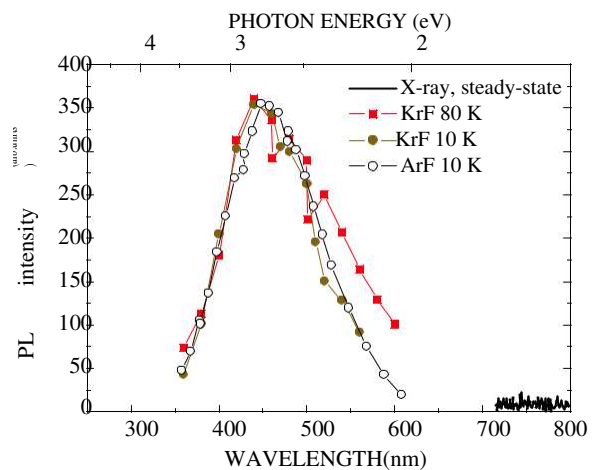


Fig. 3. Luminescence spectra of α -quartz crystal under different excitations. X-ray excitation provides STE luminescence [4]. Others types of excitations provides similar luminescence band. The spectra corresponding to excitation with lasers are time resolved.

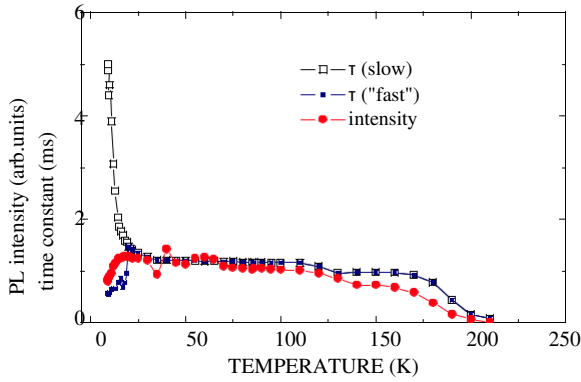


Fig. 4. Temperature dependences of luminescence intensity and decay time constants τ (slow) (1–5 ms) and τ ("fast") (~0.3 ms) of α -quartz excited with the focused beam of ArF (193 nm) laser. Separation of these two components of decay takes place below ~20 K due to zero field splitting of the STE triplet state. Details of such dependences are presented in Ref. [14]. Luminescence band is at 460 nm as presented in Fig. 3.

slow component with τ (slow) \gg 1 ms and fast component τ ("fast") ~330 μ s are connected with zero magnetic field splitting of the STE triplet state [14].

In Fig. 5 the temperature dependences of PL intensities excited with KrF (248 nm) laser excitation are compared with the case of ArF (193 nm) excitation. A good correspondence between those kinds of excitation could be noticed for the range above 80 K. Only the case of CCD spectra detection (not time resolved) using Hamamatsu mini-spectrometer is a bit shifted to higher temperature. Otherwise the temperature quenching of observed luminescence takes place near 200 K.

Analyzing the decay curves by exponential approximation in the case of KrF (248 nm) excitation we see that situation is different in the beginning and end of decay curve, Fig. 6. Although the decay curves distinguish from those excited with ArF (193 nm) laser the total quenching takes place near 200 K for the case of both lasers. We observe two components of nearly the same decay duration about 2–5 ms. Below 50 K we have a rise in decay time up to 20 ms (see also Fig. 6 insert). Integration of total decay curves also provides the temperature dependence of intensity with a rise at 50 K, however at higher temperature we observe the two-step temperature dependence, which is typical for STE. Fig. 6 shows also a temperature dependence corresponding to photoluminescence bands integration for each point of temperature. This dependence shows no rise at 50 K and corresponds well to STE temperature dependence. In the case of ArF (193 nm) two-photon excitation, Fig. 4, a monotonous increase of slow component time constant with the decrease of the temperature below 30 K takes place. It was explained as zero magnetic field splitting of the STE triplet

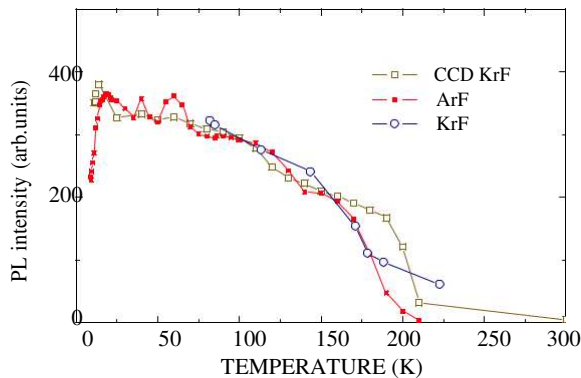


Fig. 5. Temperature dependences of time resolved blue luminescence intensity of α -quartz excited with the focused beams of ArF (193 nm) and KrF (248 nm) lasers. Data are compared with steady state measured intensity determined as integrated PL bands at different temperatures.

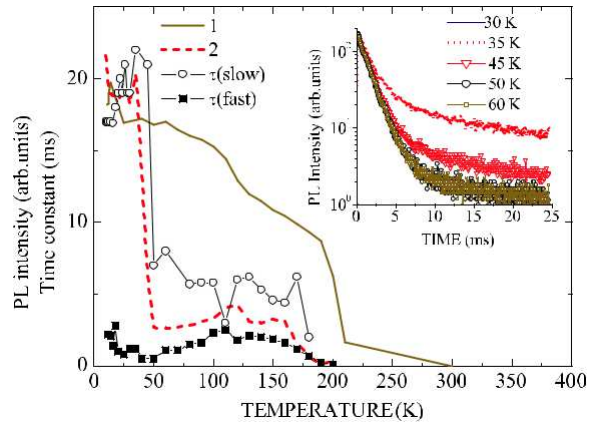


Fig. 6. Temperature dependences of the time resolved blue luminescence intensity and decay components time constants obtained by decay curves exponential approximation of α -quartz excited with the focused beam of KrF (248 nm) lasers. 1 – PL intensity obtained by integration of PL bands at different temperatures. 2 – PL intensity obtained by integration of decay curves at different temperatures, which example is presented in the insert. τ (slow) – time constant determined in the time window 10–20 ms. τ (fast) – time constant determined in the time window 0.1–2 ms. Insert demonstrates change in the kinetics at temperatures below 50 K.

state [14]. It does not correlate with the rise at 50 K in the case of KrF (248 nm) laser excitation. In the case of KrF (248 nm) excitation the analogous behavior related to triplet state splitting in zero magnetic field at 10 K was not observed. The rise at 50 K should be explained by other causes. Possibly it is manifestation of recombination luminescence.

In Fig. 7 the analyses of the fast decay of quartz crystal sample excited with KrF (248 nm) laser pulses is presented. Detection was done with photomultiplier tube H6780-04 in current regime allowing detection of fast luminescence. Laser pulse was convoluted with series of exponents and resulting pulses were compared with experimental pulse of luminescence. It could be seen that for pulses excited with KrF (248 nm) laser there is observed a fast decay component with a time constant about 3.5 ns at 80 K. The time constant decreases to about 0.5 ns at 270 K. So, the fast component is affected to temperature quenching in the same range as the slow component. Also, two-step temperature dependence takes place similarly to the STE case. However, at temperature below 50 K there is no rise for the faster component as it takes place for the slow component under KrF (248 nm) laser pulses. This agrees with the proposition that rise of the slowest component could be related to the occurrence of some recombination process below 50 K. The fast component presumed pure intra-center transitions, that is why no rise was detected in temperature

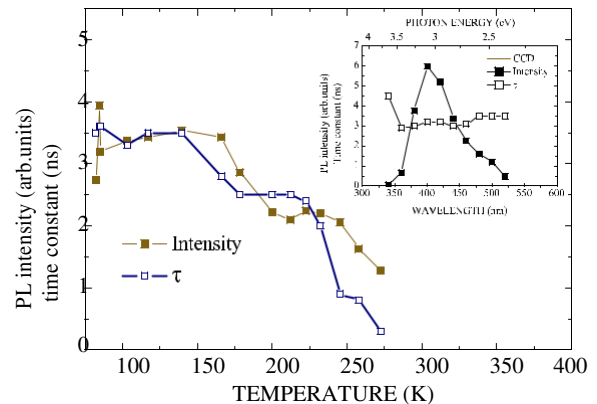


Fig. 7. Temperature dependences of time resolved luminescence intensity and fast (ns) decay time constant of α -quartz excited with the focused beam of KrF (248 nm) laser. Insert – spectral dependences of these parameters. Spectrum of steady-state PL measured at T=77 K with CCD of minispectrometer is presented as well.

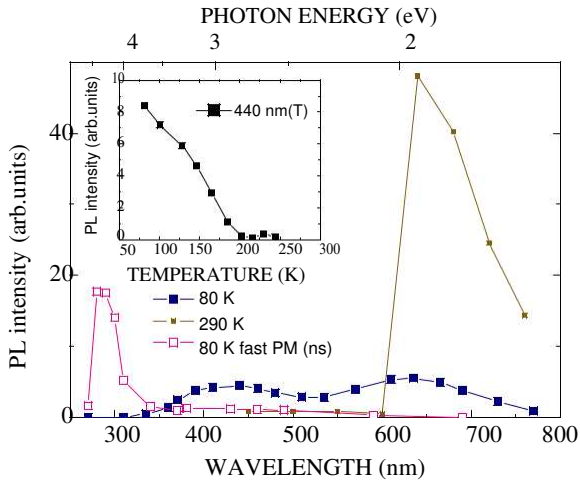


Fig. 8. Time resolved (ms and ns) PL of silica III under KrF (248 nm) pulses at 290 and 80 K. Inset – temperature dependence of time resolved luminescence intensity at 440 nm. Red luminescence at 290 K is luminescence of non-bridging oxygen created by photon stimulated detachment of hydrogen from $\equiv\text{Si-O-H}$ groups.

dependence of fast component. The temperature dependence of time resolved intensity corresponds well to that of time constant Fig. 7. In the case of ArF (193 nm) laser the fast component was also previously studied [15]. In the insert of Fig. 7 the spectral dependence of decay time constant and time resolved PL spectrum are presented. The PL spectrum measured with CCD of spectrometer is presented for comparison. The last spectrum corresponds to the luminescence in the whole range of time. So, there is a spectral shift of the band corresponding to the fast components. Slow component of STE is due to triplet – singlet transitions. The fast component is ascribed by us to singlet – singlet transitions of STE. We could ascribe this shift to the singlet – triplet splitting of STE excited with KrF (248 nm) laser. In that aspect surface related STE is similar to volume related STE excited through the two-photon process induced by ArF (193 nm) laser irradiation.

3.2. Silica glass

The Fig. 8 presents the data related to silica glass type III luminescence excited with KrF (248 nm) laser. It must be noted that in the case of ArF (193 nm) laser the strong luminescence of localized states takes place [10,13] even in silica glass type III. In the case of KrF (248 nm) laser excitation the red band due to non-bridging oxygen luminescence center (see e.g. [11]) is observed at 290 K, Fig. 8. The center is created by detaching of hydrogen from non-bridging oxygen. At 80 K the efficiency of generation of such center by pulses of KrF (248 nm) laser is reduced. Besides, the intensity of a blue luminescence increased in with cooling. Time resolved intensity's temperature dependence is presented in the insert of Fig. 8. The intensity rises monotonously with cooling as it happens for a disordered system [16]. The fast component in UV range is ascribed by us to the oxygen deficient luminescence center, which is present in small concentration in this sample. The blue band also possesses fast decay. The luminescence decay kinetics is presented in Fig. 9. It is seen that decay curves of blue luminescence are close to hyperbolic law and their shape is slightly dependent on temperature. The red luminescence decay curves are presented in insert of Fig. 9. This luminescence is also non-exponential with strong decrease of intensity with cooling. The last is evidently related to the temperature dependence of red luminescence center creation. A permanent center of non-bridging oxygen is slightly depending on temperature in the temperature range under investigation [11].

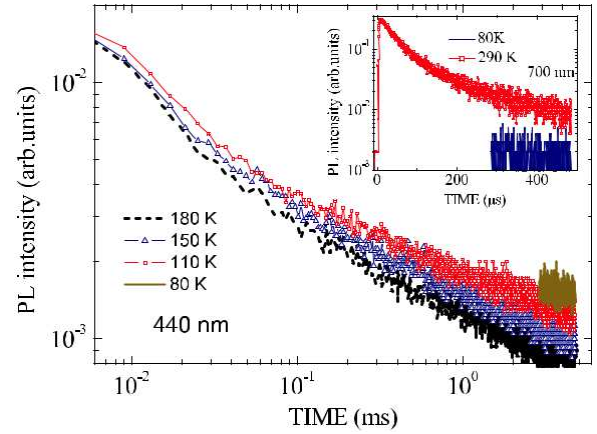


Fig. 9. PL at 440 nm decay kinetics curves at different temperatures of KrF (248 nm) excited silica of III type. Inset: decay kinetics of red luminescence of non-bridging oxygen center.

4. Discussion

Luminescence of crystalline α -quartz and pure silica glass type III was detected when excited with KrF (248 nm) excimer laser. Optical absorption is small at 248 nm, no specific bands are observed. The observed luminescence band of quartz crystal spectrally resembles that of self-trapped exciton, Fig. 3 as it is seen from the STE luminescence spectrum excited with x-rays. Also temperature quenching of the studied luminescence excited by KrF (248 nm) laser is similar to that of STE, Figs. 5–7. STE luminescence excited with ArF (193 nm) laser is presented in Fig. 4, while Fig. 5 shows comparison of intensity temperature dependences under both lasers. Temperature dependence of luminescence intensity of quartz crystal excited with KrF (248 nm) laser is similar with that of STE. Remarkable discrepancy in luminescence decay kinetic excited with KrF (248 nm) and with ArF (193 nm) laser is seen Fig. 1. There is no direct relation with the known kinetics of STE luminescence in the case of KrF (248 nm) laser. Excitation with KrF (248 nm) laser provides luminescence located in near surface area of quartz crystal sample, Fig. 2. From this we can conclude that specific properties of electronic state on the surface provide luminescence. Indeed, the level of bulk two photon absorption (TPA) for the case of KrF (248 nm) laser is about 50 times smaller than that for the case of ArF (193 nm) laser [17–19]. Therefore we practically did not see STE luminescence of quartz crystal in bulk for excitation with KrF (248 nm) laser against the background of intensive surface luminescence. Absorption for KrF (248 nm) laser photon should be assumed on some surface states of unknown nature. One can also assume the release of an electron from the surface states by a photon and hole trapping on the surface. It is known that in volume of quartz crystal a hole is not self-trapped even at 4 K [5,6]. Hypothetic self-trapped hole (STH) on the surface could explain very long duration of luminescence (rise to 20 ms below 50 K) excited by KrF (248 nm) laser. We also could assume electron self-trapping on the surface. Those self-trapped electron and hole provide STE-like luminescence on the surface with non-exponential decay probably in the recombination process. Recombination of such pair of self-trapped charge carriers in close pairs with random separation distance could provide decay time from ns to tens of ms. Rise of the kinetics parameters below 50 K could be related to the self-trapping of one of the charge carrier. However some photostimulated processes without detachment of hydrogen could take place as well. Certainly, these hypotheses need further proving.

Spectral distributions of the fast and slow components of the surface luminescence are the same, Fig. 7 insert. It is shifted to high energy side by about 0.3 eV and may be due to singlet-singlet transitions of the surface STE. So, in that KrF (248 nm) excitation case is similar to that of ArF (193 nm) excited STE in volume [15]. Small value of singlet-triplet

splitting is witnessing of STE wavefunction expanded in space. We did not observe surface luminescence excited by ArF (193 nm) laser. Probably surface state very ineffectually absorbs corresponding photons.

The situation with silica glass is different. First of all for KrF (248 nm) laser TPA of silica is slightly higher than that for quartz crystal [17,18] and here luminescence is excited also in the bulk of the sample. The luminescence of silica glass under pulses of KrF (248 nm) laser is very similar to the known STE for silica glass [8,9]. There are no differences between the new and the known data neither in band positions nor in intensity's temperature dependences. Also weak temperature dependence of decay pulse shape is similar to the known case of e-beam excitation [8]. Besides, we had observed also a fast decay of luminescence in visible range, Figs. 7 and 8. We could ascribe visible fast luminescence to singlet-singlet transitions of STE in glass. Though a self-trapped hole (STH) was found in silica as a stable defect [20], its participation in recombination process with creation of STE was not observed [9]. It was found that in silica STH efficiently recombines only with oxygen deficient defect (ODC) [10,13], which plays the role of an electron trap. The observed fast UV band at 280 nm, Fig. 8, evidently belongs to trace of ODC in spite of presence of OH groups.

5. Conclusions

KrF (248 nm) laser excitation provides luminescence of self-trapped exciton (STE) in pure samples of α -quartz crystal and silica glass type III (KY-1). STE luminescence of quartz crystal under such conditions is mainly related to the near surface area of the sample. Its luminescence band position is at 450 nm, similarly to "ordinary" STE in the bulk of sample. Temperature quenching of luminescence is similar for surface and bulk STE. Luminescence decay duration of "surface" STE possesses the fast component ascribed to the singlet-singlet transitions. The slow

component of this STE is much longer than that for the "ordinary" STE and is tentatively explained by recombination of an electron and a hole self-trapped on surface of a crystal. For silica glass the STE luminescence is excited by pulses of KrF (248 nm) laser. Red luminescence of non-bridging oxygen is created in silica type III.

Acknowledgments

This work is supported by Latvian National Program "IMIS²". We are indebted to I.I. Cheremisin for crystal samples.

References

- [1] A.N. Trukhin, A.R. Silin, I.K. Vitol, J.R. Zakis, *Izvestia Akademii Nauk SSSR (Report of Sov. Academy of Science)*, 52, 1969, 911.
- [2] D.L. Griscom, 32nd Freq. Control Symp. Electr. Indust. Assn., W-DC, 1979, 98.
- [3] A. Trukhin, A. Plaudis, 4th Conference on Radiation Phys. Chem. Ionic Crystals, University of Latvia, Rīga, 1978, 337.
- [4] A.N. Trukhin, A.E. Plaudis, *Fiz. Tverd. Tela (Sov. Sol. St. Phys.)* 21 (1979) 1109.
- [5] W. Hayes, T.J.L. Jenkin, *J. Phys. C: Sol. St. Phys.* 21 (1985) 2391.
- [6] A.N. Trukhin, *Fiz. Tverd. Tela (Sov. Sol. St. Phys.)* 28 (1986) 1460.
- [7] I. Vitols, J. Zakis, A. Silin, A. Trukhin, *Opt. Spectrosc.* 30 (1971) 115.
- [8] T. Tanaka, T. Eshita, K. Tanimura, N. Itoh, *Cryst. Latt. Def. Amorph. Mat.* 11 (1985) 221.
- [9] A.N. Trukhin, *J. Non-Cryst. Solids* 149 (1992) 32.
- [10] A.N. Trukhin, A. Sharakovski, J. Grube, D.L. Griscom, *J. Non-Cryst. Solids* 356 (2010) 982.
- [11] L. Skuja, *J. Non-Cryst. Solids* 179 (1994) 51.
- [12] D.L. Griscom, *Phys. Rev. B* 40 (1989) 4224.
- [13] A.N. Trukhin, *J. Non-Cryst. Solids* 357 (2011) 1931.
- [14] A.N. Trukhin, M. Kink, J. Maksimov, R. Kink, *Sol. State Commun.* 127 (2003) 655.
- [15] A.N. Trukhin, *J. Phys.: Condens. Matter* 20 (2008) 125217 (5pp).
- [16] C.M. Gee, M. Kastner, *Phys. Rev. Lett.* 42 (1979) 1765.
- [17] A. Dragonmir, J.G. McInerney, D.N. Nikogosyan, *Appl. Opt.* 41 (2002) 4365.
- [18] W. Ch. Mühlig, J. Triebel, *Non-Cryst. Solids* 355 (2009) 1080.
- [19] A. Dragomir, J.G. McInerney, D.N. Nikogosyan, P.G. Kazansky, *Appl. Phys. Lett.* 80 (2002) 1114.
- [20] D.L. Griscom, *J. Non-Cryst. Solids* 149 (1992) 137.