



Luminescence of phosphorus containing oxide materials: Crystalline SiO₂ P and 3 P 2 O 5 7 SiO₂ ; CaO P 2 O 5 ; SrO P 2 O 5 glasses

A. N. Trukhin, K. Smits, J. Jansons, D. Berzins, G. Chikvaidze, and D. L. Griscom

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Luminescence of Phosphorus Containing Oxide Materials: Crystalline $\text{SiO}_2\text{-P}$ and $3\text{P}_2\text{O}_5\cdot 7\text{SiO}_2$; $\text{CaO}\cdot\text{P}_2\text{O}_5$; $\text{SrO}\cdot\text{P}_2\text{O}_5$ glasses

A. N.Trukhin^{1, a)}, K. Smits¹, J. Jansons¹, D. Berzins¹, G. Chikvaidze¹,
D.L.Griscom³

¹*Institute of Solid State Physics, University of Latvia, LV-1063 Riga, Latvia*
³*impactGlass research international, 3938 E Grant Rd #131, Tucson, AZ 85712, U.S.A.*

^{a)}truhins@cfi.lu.lv

ABSTRACT. Luminescence of phosphate glasses such as $\text{CaO}\cdot\text{P}_2\text{O}_5$ and $\text{SrO}\cdot\text{P}_2\text{O}_5$ is compared with that of phosphorus doped crystalline α -quartz and phosphosilicate glass with content $3\text{P}_2\text{O}_5\cdot 7\text{SiO}_2$. Water & OH groups are found by IR spectra in these materials. The spectrum of luminescence contains many bands in the range 1.5 – 5.5 eV. The luminescence bands in UV range at 4.5- 5 eV are similar in those materials. Decay duration in exponential approximation manifests a time constant about 37 ns. Also a component in μs range was detected. PL band of μs component is shifted to low energy with respect to that of ~ 37 ns component. This shift is about 0.6 eV. It is explained as singlet-triplet splitting of excited state. Below 14 K increase of luminescence kinetics duration in μs range was observed and it was ascribed to zero magnetic field splitting of triplet excited state of the center. Yellow-red luminescence was induced by irradiation in phosphorus doped crystalline α -quartz, phosphosilicate glasses. The yellow luminescence contains two bands at 600 and 740 nm. Their decay is similar under 193 nm laser and may be fitted with the first order fractal kinetics or stretched exponent. Thermally stimulated luminescence contains only band at 600 nm. The 248 nm laser excites luminescence at 740 nm according to intra center process with decay time constant about 4 ms at 9 K. Both type of luminescence UV and yellow were ascribed to different defects containing phosphorus. P-doped α -quartz sample heated to 550 C° become opalescent. IR spectra related to water & OH groups are changed. Photoluminescence intensity of all three bands, UV (250 nm), yellow (600 nm) and red (740 nm) strongly diminished and disappeared after heating to 660 C°. Radiation induced red luminescence of non-bridging oxygen luminescence center (NBO) appeared in crystal after heat treatment. We had observed a crystalline version of this center (I. Skuja et al, Nuclear Instruments and Methods in Physics Research B 286,159–168 (2012)). Effect of heat treatment explained as sedimentation of phosphorus in some state. Keeping of treated sample at 450-500 C° leads to partial revival of ability to create yellow luminescence center under irradiation.

INTRODUCTION

Phosphorus takes on a variety of valence states in different oxides. The phosphite ion PO_3^{3-} , the orthophosphate ion PO_4^{3-} , and the pyrophosphate ion $\text{P}_2\text{O}_7^{4-}$ are among them. These ions determine different phenomena in P-doped materials. It is supposed that the PO_4^{3-} complex is main structural element in silicon dioxide doped with phosphorus. Phosphorus gives its name to one kind of luminescence – phosphorescence, however luminescence of phosphorus doped materials is not yet well studied. Luminescence of phosphate glasses was studied previously [1-3]. Two studied glasses were $\text{CaO}\cdot\text{P}_2\text{O}_5$ and $\text{SrO}\cdot\text{P}_2\text{O}_5$ possessing main photoluminescence UV band at 4 eV with hyperbolic decay. Excitation was made with spark discharge in hydrogen and detection by photon counting method [1-3]. Luminescence dependence on temperature obeys the classic rule for disordered materials: exponential growth with cooling. The luminescence has been excited in the intrinsic absorption range [1] and therefore identified as host material luminescence. Excitation with polarized light provides polarized luminescence which for disordered glass structure means excitation of localized states. Alkaline earth phosphate glasses localized states are similar with those of other oxide glasses [2,3].

Previously, UV band at 5.9 eV was found in ScPO_4 crystals. The self-trapped exciton (STE) is responsible for this band. The STE in ScPO_4 possesses singlet-singlet and triplet singlet transitions. The triplet state of STE is split in zero magnetic fields [5,6]. The singlet-triplet splitting of STE is about 0.15 eV, small this given that corresponding wave function is spread in the space, with electron component on Sc ions and hole component on PO_4 complex [7]. Actually we had found similar properties of UV luminescence in studied objects.

Phosphorus has influence on coloration of natural rose crystalline quartz [8, 9]. ESR of P doped α -quartz crystal was studied in [8, 9]. Detected were P(II) and P(I), possessing spin-1/2 hfs splitting in the ranges ~ 1080 to 1230 G and ~ 1020 to 1155 G respectively. Only P(I) has quartz-crystal symmetry. The doubly degenerate P(II) excited state has no such symmetry. Other detected defects are the P-non-bridging-oxygen hole centers (POHCs) with hfs splittings ~ 25 to 50 G. Silica glass doped with phosphorus was studied by ESR [10]. Four main centers detected were P_1 , P_2 , P_3 and Phosphorus Oxygen Hole Center (POHC). With P_2 appearing be broadened blend of the P(I) and P(II) centers in α -quartz.

Investigation of P-doped silica luminescence was performed for optical fiber preform [4]. In this case the PL band at 3 eV could be excited in the absorption bands at 4.8 and 6.4 eV. This luminescence possesses long duration with time constant about 6 ms. The luminescence center has been ascribed to P impurity substituting Si atoms in SiO_2 matrix. In studied materials of present investigation we did not found luminescence with similar parameters. We have performed luminescence studies of $\text{CaO}\cdot\text{P}_2\text{O}_5$, $\text{SrO}\cdot\text{P}_2\text{O}_5$ and $3\text{P}_2\text{O}_5\cdot 7\text{SiO}_2$ glasses as well as phosphorus doped α -quartz crystal under excitation made with excimer lasers (248 nm, 193 nm and 157 nm), deuterium discharge light source, x-ray and electron beam. We have revealed UV luminescence band similar to that of phosphate glasses as well as bands in yellow range of spectra corresponding to radiation induced defect in P-doped silicon dioxide. No data related to UV and yellow luminescence we report here for a P-doped silicon dioxide has been found in the literature and therefore that should be investigated.

EXPERIMENTAL

Phosphorus doped synthetic α -quartz crystal (~ 0.1 wt % of P_2O_5) and phosphosilicate glass of $3\text{P}_2\text{O}_5\cdot 7\text{SiO}_2$ content were the samples. The composition $3\text{P}_2\text{O}_5\cdot 7\text{SiO}_2$ was chemically stable, [11]. The α -quartz crystal was grown by hydrothermal method with adding of P_2O_5 . The sample possesses part of seed crystal which was not doped with phosphorus. The sample was γ -irradiated to dose 10^5 rad and P-doped part easily distinguished by pink coloration. Production of the samples of $\text{CaO}\cdot\text{P}_2\text{O}_5$, $\text{SrO}\cdot\text{P}_2\text{O}_5$ were described previously [1]. Pure row materials were fused in silica glass crucible. A flow of oxygen through the melt provides oxidized samples.

ArF (193 nm wavelength), KrF (248 nm wavelength) and F_2 (157 nm wavelength) excimer lasers, model PSX-100 of Neweks (Estonia) are used to excite PL. For ArF and KrF lasers pulse energy amounts to 5 mJ, whereas for the F_2 laser it is by an order of magnitude smaller. Pulse duration is 5 ns for all lasers. Luminescence emission is collected in a direction perpendicular to the exciting laser beam. Samples are carefully cleaned and mounted on a holder, no glue is used. Measurements are performed at $9 - 350$ K samples temperatures.

The measured curves are presented in figures as received therefore they reflect the level of errors. Measured decay curves were fitted to different laws by least-squares-fit method. The same method was used for other mathematical treatment of experimental results.

The sample was kept in cryostat with nitrogen screen, which allows avoid condensation of contamination film on the sample surface at low temperatures.

As x-ray source possesses W anticatode. The usual regime was 45 kV and 20 mA.

Cathodoluminescence (CL) spectra and time resolved experiments were conducted by means of pulsed electron beam equipment with electron energies 6 KeV and $0.2-1$ μs pulse duration. The fast portion of the pulse (about 1 ns) provides the possibility to measure fast kinetics.

Luminescence is detected with the help of a grating monochromator (MCD-1) with slit width of about 1 mm corresponding to 1.5 nm spectral resolution. No correction of data on experimental transfer function was made for monochromator and PM spectral sensitivity. The Hamamatsu H6780-04 photomultiplier tube (PMT) placed at the output slit of the monochromator was used as a photoreceiver. Current and/or photon counting modes of the PMT operation were used. The PMT output was loaded by a 50 Ohm resistor. The photon counting mode was instrumented with Hamamatsu H8259-02 module and was used mainly with a low intensity steady state deuterium discharge as the excitation light source. Some spectra excited by the excimer lasers were recorded with the help of this mode as well. Complimentary to the above mentioned techniques, steady state luminescence spectra were recorded by a Hamamatsu C10082CAH mini-spectrometer with a CCD camera. Spectra at 9 K were measured on Andora monochromator with CCD camera as well as with PMT, when decay kinetics curves were registered. Luminescence polarization of P-doped α -quartz crystal was measured when observation took place at 90 degrees with respect to the excitation beam of an ArF laser directed along C axis of the crystal. Excitation light of the ArF laser was unpolarized. This means that all electric vectors were in the plane of sample, whereas the beam was along

C axis. Luminescence was passed through an analyser and an optical fiber. These signals were detected with the CCD of the Hamamatsu mini spectrometer. In the geometry of the experiment, the vertical orientation of the analyser corresponded to the luminescence electric vector perpendicular to C axis and the horizontal to the electric vector of luminescence directed along C axis.

Luminescence decay curves were recorded by a Tektronics TDS 2022B oscilloscope, each curve being averaged over 128 pulses. Time-resolved luminescence spectra were extracted from the decay curves measured at each specific wavelength. Two values of the luminescence signal corresponding to nanosecond and microsecond delay times were selected for building up the spectra.

In order to correctly separate fast components from the recorded luminescence decay curves, the waveform of the excitation laser pulse was convoluted with a set of probe exponential calculated with different time constants of a nanosecond window. The calculated decay curves obtained with this procedure were compared with the ones observed in the experiment in order to properly select the best fitted decay time constant. The accuracy of this method of time constant estimation was strongly affected by a contaminating signal induced by gas discharges in a laser cavity and also depends on PMT's properties. For example, the shape of the decay curves in the vicinity of the 30 ns tick on a time axis are totally associated with a feature of the PMT functioning.

The absorption spectra were measured by two different spectrometers. The one was the Hamamatsu C10082CAH mini-spectrometer operating in a spectral range of 800 – 180 nm, the other was a spectrometer based on a 70-degree Seya-Namioka vacuum monochromator with a deuterium discharge light source. The recorded spectra were matched together at a wavelength of 220 nm. All samples contain water & OH groups absorption in IR range of spectra, Fig.1.

All recorded data are presented in the figures without smoothing. For this reason points scattering in the plots reflects inaccuracy of measurements.

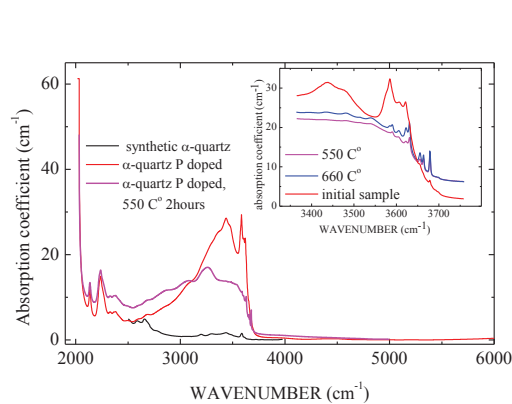


FIGURE 1. IR absorption spectra of studied sample of α -quartz doped with phosphorus. Spectrum of synthetic α -quartz, taken from [21] is presented for comparison. Heat treatment changes IR spectrum and reveals some structure. This structure, presumably, corresponds to isolated OH groups.

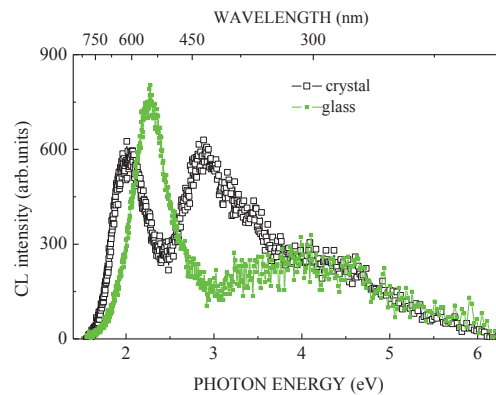


FIGURE 2. Cathodoluminescence (CL) spectra of SiO_2 -P crystal and $3\text{P}_2\text{O}_5 \cdot 7\text{SiO}_2$ glass at 293 K.

RESULTS

Cathodoluminescence

Cathodoluminescence spectra of phosphosilicate samples, crystal and glass, are presented in Fig.2 for 293 K. In both cases spectra are spread in wavelength from 6 eV (200 nm) to 1.55 eV (800 nm) containing bands in UV, visible and yellow - red part of spectra. CL of yellow - red band is decreasing during irradiation. That is explained as radiation creation-destruction of centers. After cathodoexcitation experiment irradiated place of sample is pink colored, and then corresponding centers are created. The CL decay kinetics curves are similar for both materials and possess fast repeating excitation beam pulse and slow in the range of 3-10 μs within level of noise (figure is omitted for shortening the paper).

The tail in UV part is similar for crystal and glass and, as it would be seen below, belongs to presence of

phosphorus. A band at 3 eV in the crystal could be ascribed to the remains of self-trapped exciton, which is strongly quenched at 290 K. It is almost absent in the glass due to much smaller efficiency of self-trapped exciton luminescence in silica glass [13].

X-ray excited luminescence

The yellow luminescence is not distinguished in x-ray excited spectra. Cooling to 80 K increases the intensity of visible and ultraviolet luminescence bands, Fig.3.

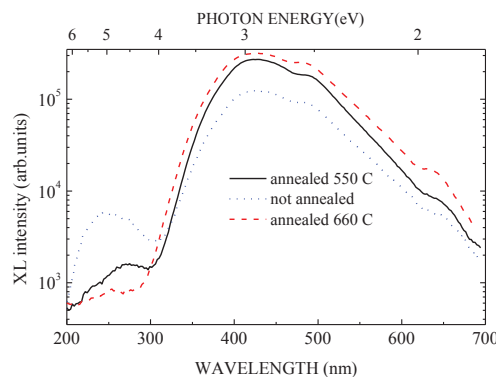


FIGURE 3. X-ray excited luminescence spectra of P-doped quartz, T=80 K. Influence of heat treatment.

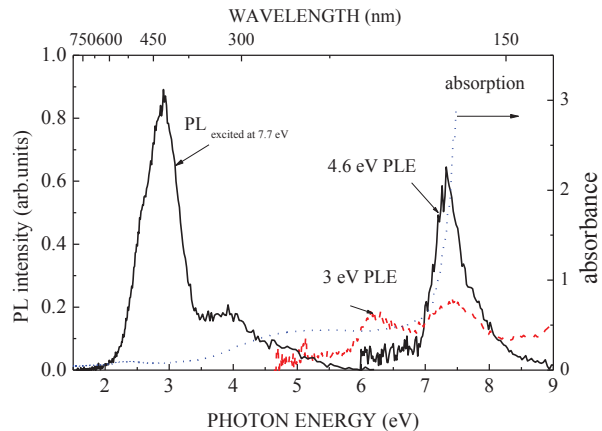


FIGURE 4. Optical absorption (right scale), PL excited at 7.7 eV and PLE detected at 4.6 eV and 3 eV spectra (left scale) of quartz with phosphorus T=80 K.

The main luminescence at 80 K is due to STEs created in the structure of α -quartz [3]. The UV luminescence at 250 nm (5 eV) was observed only in P-doped part of the sample. The Fig.3 demonstrates influence of annealing to 550 C and 660 C as for IR spectra in Fig.1. The estimated concentration is about 3500 ppm using literature data [21]. Large broad band at ~ 3400 cm⁻¹ evidently is due to presence of molecular water [21]. Absorption peak at ~ 3580 cm⁻¹ corresponds to OH groups. In the case of α -quartz crystal we performed heating of the sample at 550 C (just below α - β transition) and also at 660 C. We get significant changes in IR absorption presented in Fig.1 already with heating to 550 C. The part of sample doped with phosphorus becomes opalescence. We did not find procedure completely restoring sample properties.

The UV luminescence drops down in heated samples, whereas STE luminescence significantly increases. That could mean destruction of phosphorus related luminescence center and restore of ability provide STE luminescence. Possibly, competitive role of phosphorus centers in capturing of electronic excitations is diminished.

The STE luminescence in the glass is not as effective as in α -quartz crystal. The UV band in studied glass under x-ray excitation contains two subbands in UV one at 3.9 eV and one at 4.9 eV both strongly increasing in intensity with cooling to 80 K (figures for glasses are omitted for shortening the paper). It is assumed that both bands at 3.9 eV and at 4.9 eV belong to presence of phosphorus in phosphosilicate glass as well.

The STE luminescence does not appear in thermally stimulated luminescence (TSL) after irradiation with x-ray therefore TSL contains only defect related luminescence. The X-ray excited luminescence of the phosphate glass contains only band at 4 eV. In all three materials UV luminescence could be excited in recombination process and is observed in TSL as well.

Optical properties

In Fig.4 the optical properties of crystal doped with phosphorus are demonstrated. The detection of luminescence presented in this Fig.4 was made with photon counting method, which reflects slow component mainly (fast pulses of high intensity flow together and could not be selected). Fast components of luminescence should be studied in the

regime of registration of photomultiplier (PM) current. This will be exhibited in the data below. The optical absorption threshold related to the presence of phosphorus is started above 7 eV just below optical gap of α -quartz crystal situated at 8.5 eV at 290 K [14]. The studied sample of α -quartz with phosphorus was γ -irradiated to 10^5 Rad and therefore contains color centers possessing absorption bands at 2.3 eV and 5 eV, Fig.4. The 2.3 eV evidently is responsible for the pink coloration of irradiated sample, ascribed to presence of phosphorus early [8,9]. The UV band at 4.7 eV is mainly excited in a relatively sharp PLE band above 7 eV correlating with the beginning of sample absorption. The visible band at 3 eV also possesses PLE band above 7 eV and additional band at 6.3 eV. Those bands could be attributed to presence of phosphorus.

In the case of phosphosilicate glass we observe luminescence similar to phosphorus doped α -quartz behavior. There are both UV and visible PL bands. The optical absorption of the irradiated glass sample possesses the same induced band at 2.3 eV and 5 eV as seen in Fig.(4) for crystal. The threshold of strong absorption of glass is shifted to lower energy with respect to α -quartz and is situated above 6.3 eV.

The PL and PLE spectra of alkali earth phosphate glass are previously published [1]. The difference with above described phosphor-silicate samples in phosphate glass the only PL band is broad band at 4 eV. The excitation band of the PL at 4.6 -4.8 eV is situated at 7.6 eV well coinciding with PLE band in phosphor-silicate glass.

Excimer lasers excited luminescence

UV luminescence

Luminescence spectra of phosphorus containing samples depend on excitation source. To take advantage of this fact, we had performed time resolved spectra measurements. One experiment, made use of a pulsed F_2 laser (157 nm or 7.9 eV), which revealed a fast component, mainly due to UV bands in all three studied objects, Fig.5. However,

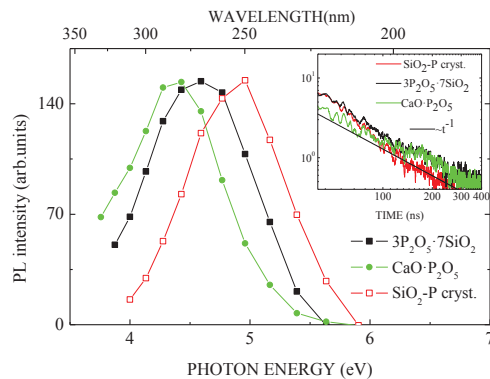


FIGURE 5. Time resolved PL spectra of studied samples with phosphorus. Intensities are obtained by integration of decay curves at corresponding photon energies. The lines are given to guide eye. Examples of decay kinetics curves are presented in insert. Line labeled as t^{-1} corresponds to the end of decay above 100 ns. F_2 laser excitation, $T=65$ K.

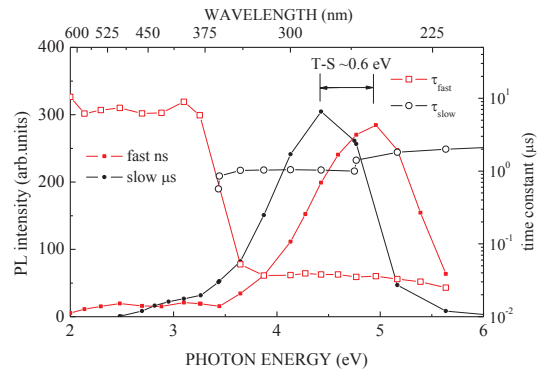


FIGURE 6. PL time resolved (left scale, close points) spectra. Intensities are obtained by integration of decay curves at corresponding photon energies. Values of τ at different PL energies are obtained by exponential approximation of decay curves (right scale, open points) of SiO_2 -P α -quartz at 9K. Excitation – pulses of F_2 laser (157 nm). Lines added to guide eyes. $T-S \sim 0.6$ eV shows estimation of triplet-singlet splitting of the excited state of UV luminescence center.

time resolved PL bands of α -quartz crystal and phosphor-silicate $3P_2O_5 \cdot 7SiO_2$ glass possess different positions (4.9 eV for α -quartz and 4.5 eV for $3P_2O_5 \cdot 7SiO_2$ glass and 4 eV for $CaO \cdot P_2O_5$ glass), all of these decay curves are close to a t^{-1} law, implying second-order kinetics (as for electron and hole recombination). After Ref. [16] the t^{-1} is a sign of tunneling recombination.

For characterization of luminescence duration we had approximated decay with exponent. In such case the fast time constant of decay is about 37 ns at 9 K (Fig.6 open squares). Fig.6 shows that decays, within the fast and slow PL bands are practically uniform, from 2 eV to ~ 3.2 eV but change dramatically above 3.3 eV, where the PL

intensity peaks at 4.4 and 5 eV for the slow and fast components respectively. This shift of about 0.6 eV is likely due to singlet-triplet splitting of excited states of a single center. Temperature dependences of time-resolved intensities and time constants are very similar in crystal, Fig.7 for fast component of decay approximate in the range of tens of ns.

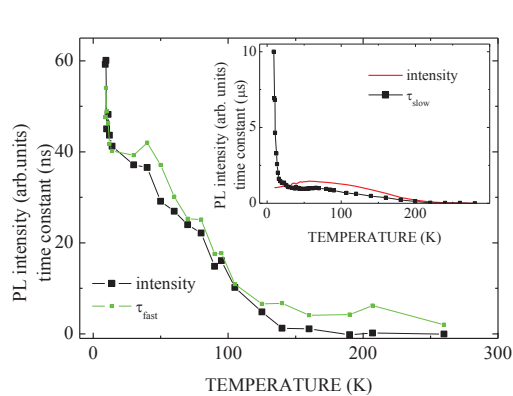


FIGURE 7. UV band time resolved PL intensity and τ temperature dependences under F2 excitation for fast and slow (insert) component of decay of phosphorus doped α -quartz crystal. Intensities are obtained by integration of decay curves at corresponding photon energies. Values of τ at different PL energies are obtained by exponential approximation of decay curves.

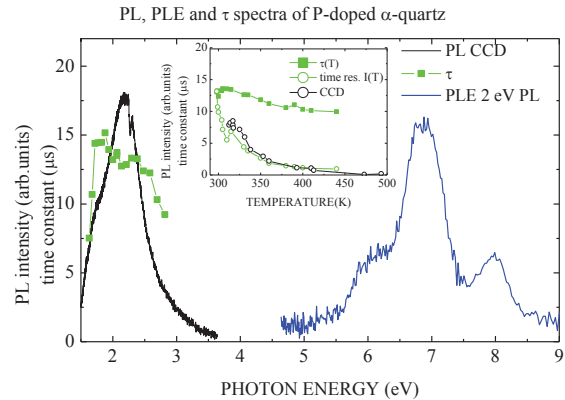


FIGURE 8. The α -quartz crystal doped with phosphorus yellow PL spectra measured with CCD camera (line) and τ obtained from exponential approximation of the decay curves measured with PM under excitation of ArF laser pulses and PLE detected at 2 eV. Insert – temperature dependences of yellow PL intensity, detected as integral under decay curve (time resolved regime) as well as detected by CCD (open points) and τ under ArF laser irradiation.

In the μ s range, shown in insert Fig.7, there is a correspondence between the intensity and the time constant within the range above 17 K. Below 17 K the decay time of the μ s component strongly increases with cooling, whereas intensity of this component changes very little. Such behavior is characteristic for a triplet state split in zero magnetic field [17].

Yellow-red luminescence

Under ArF laser (193 nm) the main luminescence is yellow-red in P-doped α -quartz crystal. It is observed both in γ -irradiated and in annealed at 700 K samples even intensity of PL is higher in annealed samples. At 293 K it is broad complex band with a shoulder in red part of spectra, Fig.8. This red band excited with KrF laser (248 nm) is presented Fig.9. Its intensity grows with cooling to 9 K in fashion presented in insert of Fig.9. The decay curves are well approximated with exponents with time constant about 4 ms at 9K, when excitation was done by KrF laser. The time constant is little changing within the band on the level of measurement errors. So, the decay is very slow. The situation with the case of ArF laser excitation is different, Fig.9. Beside red band at 750 nm there is a band at 600 nm. Visually, the luminescence of the sample is yellow under excitation with ArF laser. This band at 600 nm is little depending on temperature with cooling to 9 K, Fig.9 insert, whereas there is sufficiently good correspondence between thermal dependence of the red band at 750 nm excited with ArF and KrF lasers, Fig.9 insert. There is significant difference in the decay of the band at 750 nm under excitation with KrF and ArF lasers. Under ArF laser decay takes place in range of time up to 0.3 ms, non-exponential corresponding to empirical Becquerel law [18] $\sim 1/(1+at)^{1.19}$. That could be explained with some process of center living time limitation and participation in recombination processes.

Let go back to Fig.8. The decay kinetics of yellow band at 600 nm excited with ArF laser at 293 K could be well

PL spectrum and I(T) of P-doped α -quartz under ArF laser

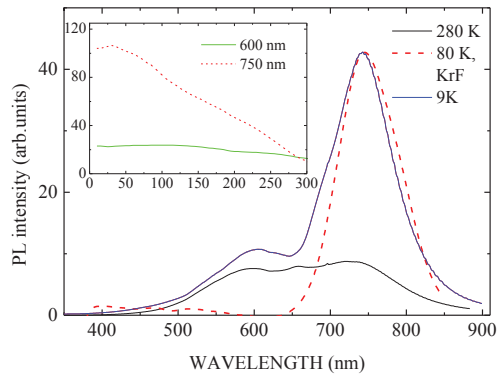


FIGURE 9. PL spectrum and I(T) (insert) measured with CCD of P-doped α -quartz under ArF laser. KrF excited PL spectrum is presented for comparison (dashed line).

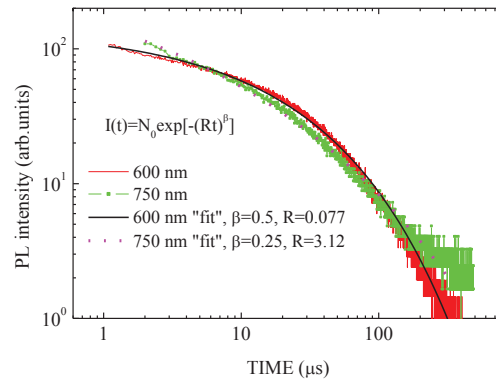


FIGURE 10. PL decay kinetics under ArF laser pulses at 9 K of SiO_2 -P α -quartz. Thick lines is 1 order fractal kinetics fitting.

approximated by exponent, Fig.8 points within PL band, and in presented insert thermal dependence of time constant and intensity. However, determined time constant is changing within the band on the level of 12 – 15 μs , Fig.8. In the same time the intensity determined by integration of decay curves and measured with CCD mutually coincide and drop down with temperature increase in different manner as that for time constant. The thermal quenching of yellow luminescence takes place at 450 K independently or intensity was measured in time resolved regime or with CCD of mini-spectrometer. The decay time constant does not follow the thermal dependence of intensity. It is little changing to 450 K. So, the quenching takes place not for radiative level but from a level feeding the radiation level. The photoluminescence excitation (PLE) spectrum of yellow band possesses the bands at 6 eV; 6.9 eV and 8 eV and was measured with photon counting method, Fig.8. Excitation spectrum contains principal band at 7 eV and additional bands at 8 and 6.3 eV. The excitation spectrum of yellow luminescence is continued to low energy oppositely to that for UV luminescence, Fig.4. Different centers should be responsible for UV and yellow luminescence.

We used also fractal approach [20] for characterization of measured at 9 K decay kinetics curves for yellow-red luminescence. The best fit was obtained for the case of first order fractal kinetics, which is characterized with stretched exponent – $I(t)=N_0 \exp[-(Rt)^\beta]$, where Rt is dimensionless time and t is real time. Result of fitting is presented in Fig.10. The only conclusion, which we able to make from this fit, is that first order fractal recombination kinetics is related to geminate pairs recombination.

The 600 nm band is main in thermally stimulated luminescence, Fig.11 obtained after x-ray irradiation at 9 K. Whereas the band at 750 nm very weak in TSL, Fig.11 insert. TSL contains many peaks (55 K, 86 K, 101 K, 192 K, 208 K and broad peak at 248 K) for 600 nm band. Significant if that the UV band at 250 nm is not effective in 55 K peak, underlining different nature of UV and yellow-red luminescence.

In the Fig.12 the luminescence intensity changes with irradiation time of ArF laser pulses are compared with the strength of ESR signal of the POHC defect, which spectrum will be presented later. The ESR signal of POHC exists in γ -irradiated sample. This center it is presumed is responsible for pink coloration of P doped samples. As ESR signal of annealed at 700 K sample grows with ArF irradiation time, the luminescence intensity exhibits different behavior, Fig.12. At 293 K we got that luminescence dose kinetics are different for γ -irradiated and annealed samples. If for γ -irradiated samples the intensity of yellow luminescence growth with dose however for annealed sample the intensity decreases with dose. It was obtained that initial luminescence intensity is higher in annealed sample than in γ -irradiated Fig.12. So, heavy irradiation with γ -ray decrease concentration of corresponding centers of luminescence.

For the case of ArF laser excitation the polarization of luminescence is different for two bands. (Not shown for

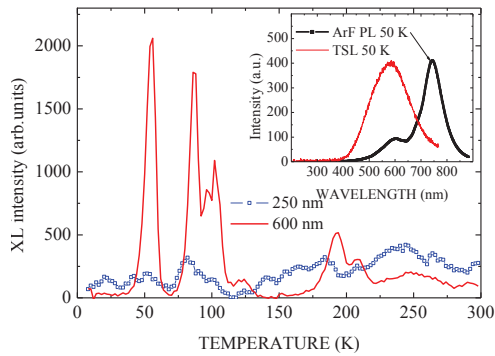


FIGURE 11. x-ray induced TSL of $\text{SiO}_2\text{-P}$ α -quartz for 600 nm (line) and for 250 nm (open points). Insert – TSL and ArF excited PL spectra in the range of TSL peak at 50 K.

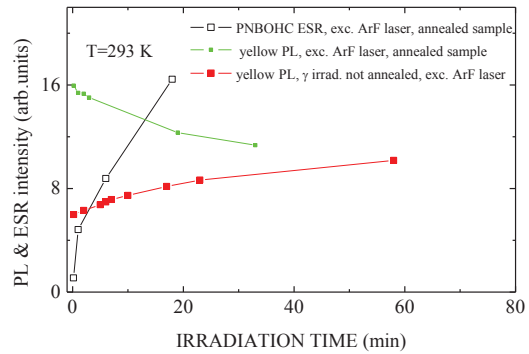


FIGURE 12. Dependences on irradiation time of intensity for yellow PL (detection with CCD) of annealed and of γ -irradiated P-doped α -quartz at 293 K, as well as that of ESR signal of POHC of annealed sample.

shortness). The band at 600 nm in the range of its maximum possesses almost zero degree of polarization in experiment described in experimental section. In the same time for the band 750 nm the emission is polarized. The geometry of experiment is that excitation with non-polarized light of ArF laser was performed along C axis and observation of luminescence was 90 degree to C axis. Vertical position of analyzer corresponds to perpendicular direction to the plane where situated excitation beam and observation direction. Correspondingly horizontal position of analyzer is parallel to C axis. The band at 750 nm is vertically polarized within geometry of experiment, having horizontal electric vector in the range of overlap with 600 nm band.

We had compared dose dependence at 80 K of yellow and UV luminescence for γ -irradiated sample and annealed sample, Fig.13. Remind that UV luminescence could be excited with photons higher than 7 eV and better is

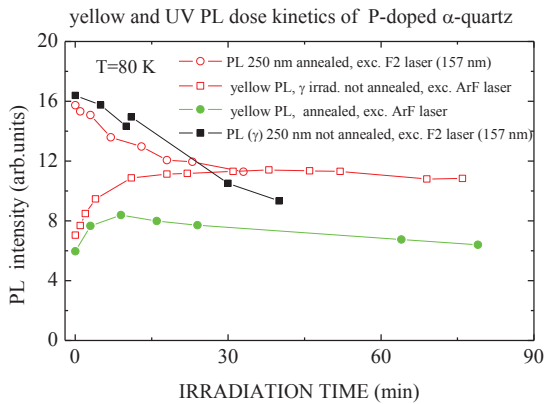


FIGURE 13. Yellow PL (circles) and UV PL (squares) (detection of decay curves with PM) dependences on irradiation time of annealed (450 C) and γ -irradiated P-doped α -quartz. The figure shows that UV and yellow centers participate in different processes.

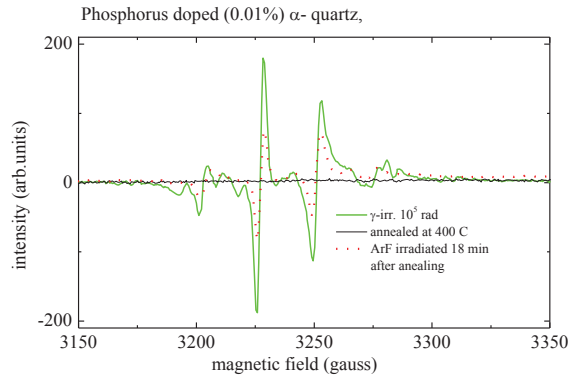


FIGURE 14. Thermal annealing of ESR spectra of phosphorus doped α -quartz and influence of ArF irradiation.

observable at low temperatures. For compared cases the UV luminescence was excited with F_2 (157 nm) laser and the yellow luminescence was excited with ArF (193 nm) laser. UV luminescence dose behavior is practically independent of annealing procedure whereas yellow luminescence dose dependence is different in annealed and not annealed (γ -irradiated) sample. It is seen that yellow luminescence exhibits similar behavior to the case of 293 K, presented in Fig.12, that in annealed sample intensity drops down with dose whereas for γ -irradiated sample little changing at high doses. Difference with 293 K is in initial part of dose curve. At 80 K intensity of yellow luminescence grows in time of ten minutes of irradiation, whereas at 293 K growth is observed only for γ -irradiated

sample, but annealed sample intensity drops down already in initial stage of irradiation, Fig.13. That could show on different processes taking place in sample at high and low temperatures for observation of yellow luminescence. Also from data in Fig.13 we can conclude that centers responsible for UV luminescence and responsible for yellow luminescence participate in different processes. Lack of TSL peak at 55 K for UV luminescence underlines this point of view, Fig.11.

ESR measurements

We possess crystal sample previously irradiated with γ -ray and there ESR signal is observed. ArF laser irradiation of phosphosilicate glass provide signal with broader band in similar place of magnetic field. This signal in the both sample, crystal and glass could be annealed at 400 C and following irradiation with ArF laser pulses partly renew the signal. Given in Fig.14 signal growth on irradiation time are presented also in Fig.12 . The ESR signal well corresponds to previously studied in [8-10] phosphorus related centers POHC. Unfortunately we were not able obtain P(I) and P(II) signal perhaps due to insufficient ability of our spectrometer.

Heat treatment of P-doped quartz crystal to 550 C° and 660 C°

Heating of α -quartz sample to 550 C°, just below α - β transition (573 C°), during two hours leads to significant changes in its properties. Part of sample activated with phosphorus become opalescent. This is witnessing on colloid formation. Spectral range corresponding to IR absorption of water and OH groups performs significant changes Fig.1. Many sharp lines appeared. Total intensity of IR absorption is diminished and the bands become broader, Fig.1. Additional heating of sample to 660 C° makes sharper lines of IR spectrum and practically destroys UV luminescence as shown in Fig.2. It could be naturally assumed that phosphorus oxide and water & OH groups are transformed to some kind of precipitation. Indeed, the optical absorption is changed. The sample surface in microscope looks as covered with some kind of puddles, which are absent on non-heated samples. Photoluminescence intensity of yellow (600 nm) and red (750 nm) strongly diminished. Practically there is no yellow luminescence after treatment. Under irradiation of ArF laser a new band at 680 nm grows. That was not observed before treatment. This luminescence also could be excited with KrF laser, but not induced with this laser. The decay kinetics of the new band is a good exponent when excited with KrF laser with time constant 17 μ s. In the case of ArF laser excitation also at 293 K, the decay is more non-exponential, and when approximated with an exponent is about 25 μ s. Seems it is evidently that non-exponential decay from one hand and creation of the center from other shows on complicated process of excitation at 293 K with ArF laser , whereas under KrF laser the pure intra-center process of excitation could be estimated. Excitation with photons of lower energy does not provide the new luminescence even previously irradiated with ArF laser. Measurement at 9 K shows that decay kinetics little changed with cooling, just seems some recombination process are frozen and under ArF excitation we observe sufficiently good exponential decay with time constant 18 μ s, insert Fig.15. PL spectrum at 9 K of the new induced luminescence exhibits good sharp lines structure with strong line at 647 nm, broad structure up to 800 nm with additional lines. No ESR signal was detected in heat treated sample after irradiation with ArF laser at room temperatures. Heat treatment to 550 C° diminishes UV luminescence in P-doped α -quartz crystal, however not completely Fig.2. Therefore it is possible conclude that UV related centers and center of yellow luminescence corresponds to different position of phosphorus in quartz. Yellow luminescence with described above properties disappear after treatment at 550 C. It could be assumed that phosphorus substituting silicon in tetrahedron corresponds to more stable UV center. However heat treatment to 660 C° practically destroys UV luminescence center. In sample heat to 660 C° NBO center was not observed after irradiation with ArF laser. Phosphorus relatively easier transforming to sediment could correspond to some structures containing P₂O₅ and water & OH groups. We had achieved some restore of heat treated sample properties, however not completely. Restoration procedure consists in keeping of treated sample at 400 C during many hours.

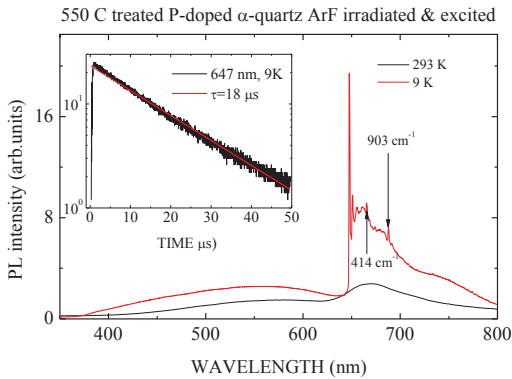


FIGURE 15. ArF laser induced PL spectra of P doped α -quartz 2 hours annealed at 550 C. Measurements are performed at 9 K under pulses of ArF laser. Sharp line at 647 nm is ascribed to zero phonon line of induced non-bridging oxygen luminescence center. Lines shifted from ZPL are 75 cm^{-1} , 414 cm^{-1} and 903 cm^{-1} . Sharp lines labeled in cm^{-1} correspond to shift of those lines from zero phonon line. Insert – decay kinetics curve under ArF laser at 9 K and exponential fit of this curve.

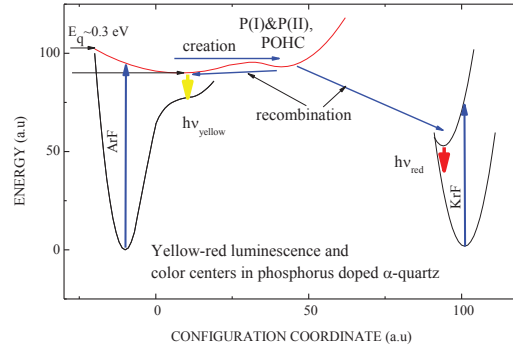


FIGURE 16. Adiabatic potential model of yellow luminescence (left side) and red luminescence (right side) and color centers (middle side). The color centers are created due to charge separation and trapping on existing defects PO_2 for trapping of electron with creation of P(I) and P(II) center and hole trapping on PO_3 with creation of POHC. Liberation of electron and hole leads to recombination process of luminescence excitation.

DISCUSSION

UV luminescence related to presence of phosphorus

Main effect of phosphorus in studied materials is creation of a luminescence center responsible for UV luminescence. It provides a broad band at 4 – 5 eV, which is sensitive to conditions of excitation and time of detection. Thus, we observe a fast component, which possesses similar thermal behavior in P doped α -quartz crystal and phosphor-silicate glass. The nature of electronic transitions in the center responsible for UV luminescence in studied materials could be explained as intra-center transitions. Indeed, in the case of P doped α -quartz crystal, there is correspondence between thermal dependence of intensity and decay parameters, Fig. 7. In the case of phosphate glasses, the reason is observed in [1] polarization of luminescence for excitation with polarized light. In the case of phospho-silicate crystal and glass, the intra-center nature of the transitions could be argued by observation of slowing decay and increasing intensity for decreasing temperature. The behavior of recombination luminescence should be opposite. If the nature of luminescence excitation process could be recombination of electron and holes, the decreasing temperature should slow down decay duration and decrease luminescence intensity. So, experimental data underline the intra-center nature of electronic transitions. Using exponential approximation, we were able to compare PL intensity and time constant thermal dependences, Fig. 7. The effects related to singlet and triplet states were discovered. These are the zero magnetic field splitting of the triplet state and singlet-triplet splitting of the UV PL band. In this, our studied phosphorus-containing materials correlate with the observation of singlet-triplet nature of self-trapped exciton luminescence in scandium orthophosphate [5, 6]. The STE in scandium orthophosphate was assumed as a hole component on PO_4 tetrahedron, whereas the electron spread over scandium. A similar model of UV luminescence center created by phosphorus in silicon dioxide could be proposed. The excited state of this center could be imagined as an electron transition from PO_4 tetrahedron to states of silicon. Remarkable is that heat treatment of P-doped quartz to 550 C does not destroy completely UV luminescence. Oppositely, this treatment completely removes yellow luminescence and strongly affects IR absorption related to water & OH groups. Therefore, the corresponding UV luminescence center should be connected to phosphorus situated in a position far from water & OH groups. In that UV luminescence center is similar to UV luminescence of ScPO_4 , where water & OH groups were not observed by direct measurement of IR absorption.

In the case of studied glasses, where the concentration of phosphorus is high, some additional peculiarities may be observed in the case of disordered materials. That is structural non-equivalence of centers with corresponding

transformation of single decay kinetics (exponent) to a wide distribution of parameters.

Center responsible for UV luminescence participates in recombination processes. It is seen in thermally stimulated luminescence, Fig.11.

Yellow-red luminescence related to presence of phosphorus

It is discovered existence of yellow-red luminescence. Corresponding centers are radiation induced. The intensity of yellow luminescence is sensitive to duration of irradiation with ArF laser Figs.12, 13. The yellow luminescence is excited at energies lower than excitation energy of UV luminescence, therefore corresponding luminescence should belong to others phosphorus related defect than defects responsible for UV luminescence.

Yellow-red luminescence possesses two bands at 600 nm (yellow) and at 750 nm (red). Both bands are excited with ArF laser (193 nm) mainly in recombination process, whereas KrF laser (248 nm) excites only red band in intra-center process. In pure recombination process, which provide by observation of thermally stimulated luminescence (TSL) mainly band at 600 nm is observed after ArF laser irradiation at 9 K. Yellow luminescence drops down in annealed sample with dose contrary to radiation induced pink coloration and corresponding signal of POHC or hole trapping center, which grows up with irradiation dose. So, however yellow-red luminescence is induced with radiation it dose behavior is different than color center or POHC ESR and yellow-red luminescence center is not the same as POHC.

From literature [8, 9] it is known that in crystalline quartz with phosphorus another defect seen on ESR as P(I) and P(II) which corresponds to two different states of one defect trapped an electron. Unfortunately we were not able detect those centers in our experiment may be due to not good properties of our spectrometer, but we presume that these centers exist after irradiation. We could expect them as electron traps. The P(I) has quartz-crystal symmetry. The doubly degenerate P(II) excited state has no such symmetry [8, 9]. That correlates with observation of luminescence polarization the luminescence band at 750 nm polarized perpendicularly to C axis corresponds to P(I) center and luminescence band at 600 nm having non polarized luminescence in the range of maximum corresponds to P(II) center.

Let us consider model responsible for yellow luminescence on the base of crystalline α -quartz doped with phosphorus, Fig.16. The precursor of POHC could be PO_3 . Presence of water in the sample would resolve charge compensation problem. Production of yellow luminescence center anti - correlates with color center production. The recombination center does not directly bond to those radiation defects.

However it is assumed that the center exists in annealed sample, we did not observed this center with low energy excitation, N_2 laser or 337 nm and 533 nm lasers, for example. That is reflected in the model Fig.16 as emission takes place after strong relaxation in defect. Stokes shift from excitation to PL band position is high and possibility to observe PL under lower energy excitation should not be obtained. Then it looks as this center is produced with irradiation and exists as only transient center in some stage on the way of creation permanent color center. That we reflect on the model describing yellow-red luminescence as existence of a specific form of ground state adiabatic potential presuming deep relaxation from equilibrium of ground state coordination coordinate that emission takes place for defect strongly transformed from defect absorbing irradiation photons, Fig.16. After emission of yellow luminescence the initial defect was restored. The model Fig.16 reflect that red band belongs to another defect providing red luminescence in pure intra center process, because of observation of luminescence with pure exponential decay ($\tau=4$ ms at 9K). Both defects are feeding from electron-holes traps, however in different process. The band at 600 nm could appear pure recombination process (TSL) and the 750 nm band appears in process of close pair tunneling recombination. During recombination limitation of living time of the 750 nm center are observed. The component of 4 ms does not takes place under ArF laser excitation.

Short range of time undistinguished from intra-center processes, presumes short distances between electron and hole traps and therefore these traps could not be exactly P(I), P(II) and POHC, because they precursors could not be close to each other. Also, however thermal quenching of yellow luminescence takes place at high temperature above 450 K, in time of annealing to high temperature (450 °C or 550 °C) we did not observe yellow TSL. So yellow luminescence is not connected directly with recombination of POHC and P(I) and P(II) centers, but they could provide electron and hole for feeding of the recombination center.

So, we have to assume existence of electron and hole traps within nearest coordination spheres of the recombination center responsible for yellow luminescence.

Also the range of time is not usual for recombination process and we did not observed usual effect related to recombination process. That is intensity drops down and decay duration increase with cooling. We did observed, Fig.9 little dependence of intensity in the range of temperature below 50 K for both component of yellow PL at 600 nm and 750 nm.

Existence of two sub bands of yellow luminescence shows on multiform of yellow luminescence center. Decay kinetics and intensity behavior is like intra center, whereas decay law is as recombination. Fractal kinetics analyses, Fig.10, show that recombination is of first order fractal kinetics and then recombination takes place for geminate pairs.

Therefore we have some controversial data – from the one hand, we have obviously recombination process of yellow luminescence excitation expressed by non-exponential law of decay and, from the other hand, we did not observe anti correlation of intensity, dropping down with cooling in the case of pure liberation of charge from traps, moving and recombination on recombination center, and luminescence duration, which should increase with cooling in pure recombination process. Then we have to assume that charge separation under ArF laser takes place within first's coordination spheres of the place absorbing excitation photon. Thus is in good agreement with fractal analyses of kinetics witnessing on recombination of geminate pairs. When such separation took place the recombination center is created and yellow luminescence appears as not pure recombination process and not pure intra center process. Further separation of the charge carriers leads to creation of traps responsible for TSL peaks. We have to assume that there is a stage of continuing process of charge separation leading to creation of permanent defect responsible of pink coloration observed in all studied samples under ArF laser excitation.

Heat treatment at 550 C, evidently, activates water & OH groups movement and reconstruction of defect precursor, then observed previous luminescence bands are, at least, diminished. After analyses of sample in microscope the surface is covered with puddles. It looks as phosphorus in some state together with OH groups and water molecules is detached from α -quartz lattice moved to interstitial position and even creates puddles on the surface. Instead of yellow luminescence the radiation induced luminescence of non-bridging oxygen luminescence center appeared. This center is known from studies of pure silica glass with significant influence of inhomogeneous broadening. We had observed a crystalline version of this center –less affected with inhomogeneous broadening and zero phonon line at 647 nm with phonon repetitions, Fig.14 shifted to 903 cm^{-1} , 414 cm^{-1} were easily observed under ArF laser excitation at 9 K. (we could not explain line shifted from zero phonon line on distance and 75 cm^{-1} , possibly that this line is a zero phonon line of a modified NBO.) So, we can assume that some OH groups on voids of transformed lattice after part of water and OH groups together with phosphorus comes to some interstitial positions. Precipitations are created including phosphorus and water. The phonon repetition at 903 cm^{-1} non-bridging oxygen luminescence center could corresponds to stretching mode of Si-O local vibration, similarly to 890 cm^{-1} in the case of silica glass [20]. If NBO could be related to phosphorus the phonon repetition should be situated about 940 cm^{-1} , correspondingly to higher weight of phosphorus [23]. Also the value of NBO luminescence time constant equal to $17\ \mu\text{s}$ is similar to NBO connected to silicon both in silica glass and neutron irradiated α -quartz crystal [23]. The repetitions at 414 cm^{-1} should find it explanation later. This center is related to crystal part. Probably this is part of crystal from which phosphorus of divided into precipitations. Remaining part with OH groups could provide non-bridging oxygen luminescence center by removing of H into other position with stabilization at RT. Significantly, that treatment of the sample at 660 C does not provide ability for NBO luminescence center creation.

CONCLUSIONS

Three types of luminescence centers are observed in phosphorus containing oxides: phosphate glasses, phosphosilicate glasses and α -quartz silicon dioxide crystal doped with phosphorus. Corresponding bands are situated in UV, visible and yellow-red ranges of spectra. UV luminescence is provided by center existing in as received materials and ascribed to the states related to PO_4^{3-} ion based on similarity of UV luminescence with STE luminescence in ScPO_4 crystal. Yellow luminescence belongs to radiation induced transient centers connected with presence of phosphorus, but structure of this center is not yet clear. The same unknown structure is for red luminescence center, also belonging to presence of phosphorus. These centers participate in electron hole recombination process in different ways. The band at 600 nm could be excited in over barrier recombination whereas 740 in tunneling recombination. Annealing of crystal sample at $550\text{ }^\circ\text{C}$ reconstructs phosphorus position. It diminishes UV luminescence, however yellow luminescence completely disappeared. ArF irradiation induces non-bridging oxygen luminescence center in crystalline lattice after treatment to $550\text{ }^\circ\text{C}$. This center corresponds to

phosphorus which position could be diminished in quantity by heat treatment to 660 °C. NBO could not be created by irradiation after treatment to 660 °C. Heating at 450 °C – 500 °C of treated samples partly recover ability to create yellow luminescence centers. Evidently, water, existing in the sample, changes its position and restoring in some way initial defect's precursors.

Radiation induced non-bridging oxygen quasi molecular center, possesses zero phonon line and phonon repetition of this line at low temperature. The parameters of phonon repetition band correspond to non-bridging oxygen connected with silicon and not with phosphorus.

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