Photoluminescence excited by ArF and KrF lasers and optical absorption of stishovite mono-crystal

Photoluminescence excited by ArF and KrF lasers and optical absorption of stishovite mono-crystal

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Abstract
Two photoluminescence bands were found in a stishovite (silicon dioxide) mono-crystal sample under ArF (193 nm) and KrF (248 nm) excitation. The blue band is situated at 3.17 ± 0.02 eV in the case of ArF and at 3 ± 0.2 in the case of KrF. The UV band is at 4.55 ± 0.05 eV in the case of ArF and at 4.5 ± 0.05 eV in the case of KrF. The position of the UV emission band correlates with that excited by x rays. This position is 4.6 ± 0.05 eV with FWHM 0.8 ± 0.05 eV (Truhins *et al* 2003 *Solid State Commun.* **127** 415). The blue band possesses slow decay kinetics with time constant 16 ± 2 μs and the UV band is fast on the level of 2 ± 0.5 ns, similarly for both lasers. Thermal quenching of both bands begins for T higher than 150 K. The activation energies are similar for intensity and time constant, and are equal to 0.23 ± 0.01 eV and 0.13 ± 0.01 eV for blue and UV bands, respectively, with equal values of frequency factor, 2×10^{11} s^{-1}. Optical absorption contains bands at 4.5, 5.5, and 7 eV and a strong band starting from 7 eV adjacent to the intrinsic absorption threshold above 8.75 eV. Excitation at 7.86 eV (F$_2$ laser) does not provide luminescence. The nature of the luminescence excited in the transparency range of stishovite is ascribed to a defect, presumably created by previous irradiation of the crystal. Similarity of the stishovite luminescence to that of oxygen-deficient silica glass and also to that induced by irradiation of α-quartz crystals allows us to conclude similar natures for the defect centers in these dissimilar materials.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

An important problem concerning the physics of silicon dioxide is defect absorption in the range of 7.6 eV in as-received silica glass, which is generally related to oxygen deficiency of glass. The absence of this band in crystalline α-quartz with similar luminescence properties as silica glass is intriguing. Scientists have been trying to resolve this problem for several tens of years (see, for example, review articles [1, 2]). Investigation of germanium dioxide, at the same time, has revealed considerable parallelism with the properties of silicon dioxide. Similar oxygen-deficient luminescence centers exist in germanium dioxide glass [3], whereas it is absent in germanium dioxide with α-quartz structure. On the other hand, germanium dioxide crystals with rutile structure manifest luminescence centers with almost identical properties to centers in germania glasses obtained from the same fusion process as used for crystal growth [4, 5]. This has stimulated us to perform a series of investigations of stishovite, a crystalline polymorph of SiO$_2$ with rutile structure [6–8]. However, the small dimensions of the typically obtained mono-crystals makes these experiments difficult. Initially, we were able to measure only x-ray and cathode excited luminescence, which revealed the existence of a broad

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UV luminescence band at 4.6 eV [6]. Subsequently, we were able to measure the position of the intrinsic absorption threshold in stishovite as being the highest recorded (8.75 eV) in the family of silicon dioxide materials [7]. This result differentiates silicon dioxide from germanium dioxide, since rutile-structured germanium dioxide possesses the lowest absorption threshold (4.6 eV) [9] among germanium dioxide materials. This observation became the basis for proposing varying roles for octahedral structures in germania glasses that possess two absorption thresholds, one at 6 eV, coinciding exactly with the threshold position in germania crystal with α-quartz structure, and another at 4.6 eV, coinciding with the threshold in rutile-structured GeO_2 [10]. The next step was made in [8]. The luminescence band at 4.6 eV, x-ray excited, was compared with the cathodoluminescence of silicon dioxide in the α-quartz form. In the latter, lattice-damaging irradiation induces at low temperatures (60–5 K) a UV luminescence band at 4.9 eV. This band grows with dose from zero level [11]. The effect was interpreted [11] as creation of a certain defect in α-quartz by dense cathode irradiation that is similar to the defect of stishovite that gives rise to the UV luminescence band. The defect created by electron-beam irradiation of silicon dioxide α-quartz crystals is unstable above 80 K. Previously, a spectroscopically similar but stable defect was produced in α-quartz at room temperature by gamma and neutron irradiation [12, 13]. The latter defect was interpreted as an oxygen-deficient center associated with parts of the crystal that had been amorphized by these radiations. The induced defect in α-quartz could be excited by photons in the range of the 7.6 eV band [13].

Since up to this moment stishovite photoluminescence (PL) excited in the transparency range of the crystal has been poorly understood, we have performed a search for photoexcited luminescence in a stishovite mono-crystal. From the literature it is a known fact [14] that polycrystalline stishovite possesses photoexcited UV luminescence in the high energy range above the intrinsic absorption threshold determined in [7]. In our new experiments we have used as excitation sources synchrotron radiation and F_2, ArF and KrF laser photons. We have failed to detect any luminescence of the mono-crystal under synchrotron radiation or F_2 laser photons. It is not currently possible to say whether this negative result represents an intrinsic property of the material or is just a result of difficulties with alignment. In any event, we succeeded in detecting photoluminescence in stishovite under KrF and ArF laser excitation, and this article is dedicated to reporting these results.

2. Experimental procedure

The stishovite mono-crystal was grown under hydrothermal conditions by methods published in [15, 16]. The samples of this investigation were small optically transparent mono-crystals with dimensions about $0.4 \times 0.2 \times 0.2$ mm^3. The sample was held on a copper holder covered with an indium layer possessing a hole. The sample was pressed into the hole, using a procedure carried out under a microscope. The holder with the sample is shown in figure 1. The excitation light
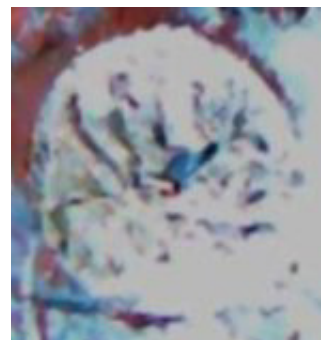

Figure 1. Sample holder with sample. The circle is of diameter 3 mm and contains soldered indium, which the sample is pressed into. The sample is the small transparent rectangle in the middle of the circle.

was passed through the hole in the holder and the detector was located on the other side, so as to exclude possible luminescence of contamination on the front surface of the holder.

The optical absorption was measured with a Hamamatsu mini spectrometer and an optical fiber, using a deuterium discharge lamp as the light source. The measured spectrum was sewn together with a spectrum previously measured in the vacuum ultraviolet range [7].

The KrF, ArF and F_2 lasers (model PSX-100, made by Neweks, Estonia) were excitation light sources. The F_2 (157 nm) has a pulse energy of about 0.5 mJ with a duration of 5 ns. The KrF (248 nm) and ArF laser (193 nm) were of 10 times higher power. The laser was situated 1 m distant from the sample. The laser beam was 2×2 mm^2 on output and became 4×4 at the sample. We did not use a focusing lens; the recorded luminescence was excited mainly as a single-photon process. A crystalline silicon dioxide crystal with a low level of luminescence was used as a window to pass the light of the excitation lasers into the sample chamber. A cryostat maintained the sample temperature in the range 60–350 K. Luminescence detection was realized by means of a grating monochromator, MCD-1, having both slits about 1 mm and a photomultiplier tube H6780-04 with 50 Ω resistive load. The resolution of the MCD-1 could not be improved by making the slits smaller because the sample has such small dimensions and therefore would not pass sufficient light intensity for high-resolution measurements. Optical filters were employed for cutting undesirable light in the line for luminescence detection. UFS1 (cut at 5 eV) and UFS2 (cut at 4.6 eV) were used for ArF and KrF respectively for measurement of the UV luminescence band. Distortion of the luminescence spectra by the filter in this case was corrected. The correction curve was obtained from comparison with the luminescence spectrum of a silver-activated crystal α-quartz (the PL band at 4.75 eV) measured with and without UV filter. A BS8 filter was used for measurements of the blue band. An oscilloscope (Tektronix TDS 2022B) was exploited for decay curve registration. The time-resolved spectra are measured by registration of the decay curve for each point of the PL spectrum in two time ranges—one in the nanosecond range and the other in the microsecond range.
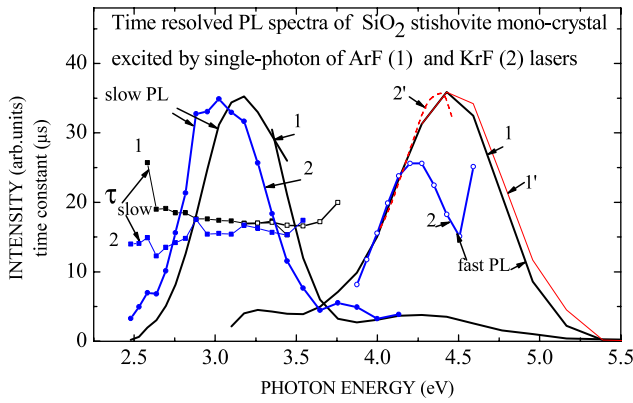
Figure 2. Time-resolved PL spectra and decay time constant of the slow component of a defect in an SiO2 stishovite mono-crystal excited by a single photon of ArF (1) and KrF (2) lasers. $T = 80$ K. Spectra $1'$ and $2'$ corrected for optical transmission of the UFS filters.

Figure 3. Optical absorption spectrum of the stishovite mono-crystal. Lines show position of the utilized laser photon energies.

3. Results

Time-resolved PL spectra are presented in figure 2 for fast (2 ± 0.5 ns) and slow (16 ± 2 μs) components of decay of stishovite mono-crystal. The UV band is at 4.5 eV in the case of ArF excitation and at 4.3 eV in the case of KrF. The blue band is situated at 3.17 ± 0.02 eV in the case of ArF and at 3 ± 0.2 eV in the case of KrF. The optical filter used for cutting second-order light passing through the grating monochromator and the diminishing influence of the first-order KrF laser light distorts the shape of the UV band. The effect is especially strong in the case of KrF laser excitation, since the line is very close to the luminescence and the filter does not cut excitation light completely. For ArF and KrF different filters, the UFS-1 and UFS-2, were used correspondingly. The corrected spectra are presented as well in figure 2, curves $1'$ and $2'$, and after correction the UV band position for the case of KrF excitation is shifted to 4.5 eV. However, this correction cannot be considered as complete, because the UFS2 filter used here entirely cut light above 4.6 eV, where luminescence could possibly take place. Thus, the true position of the UV band is likely to be more shifted to the higher energy side. The real position of the UV band should be taken from the case of excitation without stray light. This was done previously under x-ray and cathodoexcitation, and the UV band position found in this way is 4.6 ± 0.05 eV with FWHM 0.8 ± 0.05 eV [6–8]. The filter used for the blue band range was the same for both lasers, and this filter did not distort the shape of a band in this range. Therefore, the shift in blue band position currently reported under different laser excitation wavelengths is real.

The time constant is insensitive to excitation wavelength within the blue band, and its value is 16 ± 2 μs (figure 2). The decay kinetics curves are presented in figure 4, where it is seen that blue band kinetics curves are accurately exponential. The UV band possess two components, a fast and a slow. The slow component is of very low intensity. Its exponential behavior can only be ascertained to $\sim$90 μs. A component exhibiting the same luminescence kinetics under cathodoexcitation has been reported previously [6]. The duration of the fast
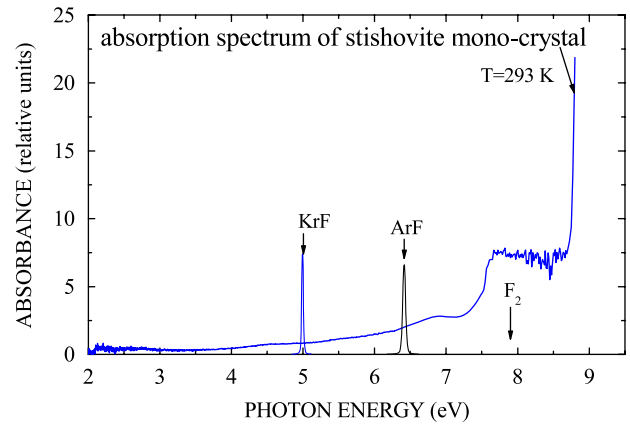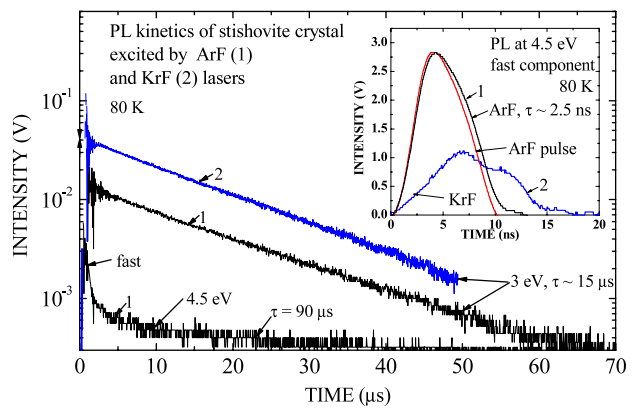

Figure 4. PL kinetics of stishovite crystal excited by ArF (1) and KrF (2) lasers. Inset: PL at 4.5 eV, fast component. $T = 80$ K.

component is practically identical with that of the excitation pulse, and its decay time constant determined by deconvolution is about 2 ± 0.5 ns. Observation of fast PL correlates with previous observation of the fast component in cathode luminescence [6–8].

The optical absorption spectrum of the sample of stishovite mono-crystal is presented in figure 3. Figure 3 shows an absorption band near 4.5 eV; however, we have not yet tried to excite PL there. The positions of the laser lines used for excitation of PL are shown as well. The F2 laser does not provide luminescence in our experiment, despite its coincidence with a strong absorption band above 7 eV. The ArF laser line falls to the low side of an absorption band at 6.9 eV and the KrF laser line falls to the low side of an absorption band at 5.5 eV, where there is either a shoulder on the absorption spectrum at 5.5 eV or a separate band near 4.5 eV. Measurement of PL of stishovite poly-crystal does not reveal a UV PL band for excitation at 6–8.8 eV, where only visible bands are excited [14]. We did not see even a blue band in our case. The UV band, situated at 4.4 eV, is excited only above the intrinsic threshold for this sample [8].

The temperature dependences of time-resolved PL intensity and decay time constants are presented in figure 5. There is a correspondence between decline of PL intensity and
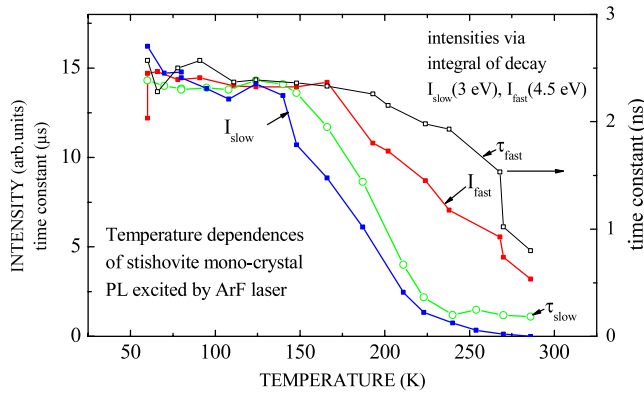
Figure 5. Temperature dependences of the stishovite mono-crystal PL excited by an ArF laser. Intensities via integral of decay I_{slow} (3 eV), I_{fast} (4.5 eV). Decay time constants are shown for the slow blue band and the fast UV band.

decay time constant with temperature; however, the decline of the time constant is retarded with respect to intensity. We estimate the parameters of quenching using Mott's expressions for this: $I(T) = I_0(1 + \tau_0 f \exp(-E/kT))^{-1}$ and $\tau(T) = \tau_0(1 + \tau_0 f \exp(-E/kT))^{-1}$, where I and τ are the intensity and time constant correspondingly. I_0 and τ_0 are non-quenched parameters. E is the activation energy and f is the frequency factor of the quenching process.

The activation energies are similar for intensity and time constant, and are equal to 0.23 ± 0.01 eV and 0.13 ± 0.01 eV for blue and UV bands, respectively, with equal values of frequency factor, 2×10^{11} s^{-1}.

So, both luminescence bands are excited in the same absorption band and their thermal quenching curves are started in the same temperature range.

4. Discussion

We have observed two luminescence bands excited in the optical transparency range of a silicon dioxide stishovite mono-crystal in a single-photon process with 4.97 eV (KrF) and at 6.4 eV (ArF) photons. These bands are situated in the blue (3–3.1 eV) and UV (4.5 eV) range of spectra. The filters we were compelled to use distorted the measured position of the UV band; however, the real position of the UV band was determined in the x-ray excited spectrum to be at 4.6 ± 0.05 eV, with FWHM 0.8 ± 0.05 eV [7, 8]. The decay time constants are slow (16 ± 2 μs) for the blue band and fast (2 ns) for the UV band at low temperature. Thermal quenching takes place above 150 K for both bands. The activation energies were 0.23 ± 0.01 eV and 0.13 ± 0.01 eV for blue and UV bands, respectively, with equal values of the frequency factor 2×10^{11} s^{-1}. So, we have two PL bands excited in an intra-center process. Observation of a component with a 90 μs decay time for the UV band under an ArF laser agrees with a previous study of stishovite mono-crystal luminescence under ionizing radiation. So, the appearance of this same component under laser excitation is ascribed to recombination luminescence of low yield. Thus, in spite of expanding the laser beam to a big

spot at a distance of 1 m, it appears that a low yield two-photon process is possible.

Let us discuss the nature of luminescence. The conclusions of previous investigations say that the 4.6 eV PL band gradually appears in stishovite during irradiation, growing with increasing dose due to defects created by radiation. Accumulation of these centers is observed on multiple cooling–heating cycles. The 4.5 eV UV band of stishovite is compared with the 4.9 eV luminescence band in α-quartz [11]. This band is fast in photo-excitation ($\sim$1 ns [17]) and the UV bands of both damaged α-quartz and damaged stishovite crystals are comparable with the fast UV luminescence of oxygen-deficient silica glass. In the latter case two luminescence bands are discovered there (see e.g. [1, 18]), a blue band at 2.7 eV with slow (ms) decay and a UV band at 4.4 eV with fast (4.5 ns) decay. These bands both belong to the same defect, due to the triplet–singlet (slow) and singlet–singlet (fast) transitions. Both in oxygen-deficient silica and the stishovite mono-crystal both luminescence bands are easy to excite in the range of 5 and 6.4 eV. Possibly in the case of stishovite we also have one defect with two luminescence bands, but the situation does not show complete similarity, since the UV bands differ in the three cases mentioned. The properties of the blue PL band are not well comparable in stishovite, irradiated crystalline α-quartz, and silica glass. The blue band was not observed in x-ray excited stishovite [7, 8], whereas the blue band of irradiated crystalline α-quartz possesses the main fast luminescence [13, 17, 19]. The nature of the blue band in these materials needs further investigation. The UV PL band of α-quartz crystals is associated with transient centers created by destructive electron-beam irradiation or permanent centers created by neutron or γ-irradiation [12, 13]. Heavily damaged α quartz is a candidate for an oxygen-deficient center of luminescence analogous to that of silica glass [1, 2]. On the other hand, the induced centers in the α-quartz crystal are very similar to the centers observed in the stishovite mono-crystal [8]. As a result of heavy bombardment, the packing of the α-quartz lattice becomes locally more compact, the co-ordination of silicon is changed, and similar defects in stishovite-like clusters are created [8]. Presumably, in the stishovite structure, such a defect is created more easily just by removing oxygen to an interstitial position. Therefore, it is very probable that the observed defect in this work is created by previous ionizing irradiation, when the sample was studied by cathode luminescence and x-ray excited luminescence. For an answer to this question, it will be necessary to study PL in a virgin (non-irradiated) sample.

So, we observe similarities between the UV PL bands of three materials, irradiated quartz, stishovite and oxygen-deficient silica glass. In all three cases the UV band is very fast and excited in the transparency range of the material.

The absorption band is at 7.7 eV in the stishovite mono-crystal. It could be a basis for understanding the analogous band in oxygen-deficient silica glass. There is a similarity of the behavior of the defect related to the 7.7 eV absorption band with that in silica glass [1, 2] and also with the induced absorption band in α-quartz [12, 13, 17], however with

significant differences. We failed to observe PL by F_2 laser excitation of stishovite. Also in oxygen-deficient silica, the yield of luminescence excited in the 7.6 eV absorption band is low. In contrast, the PL of both bands of irradiated α-quartz is mainly excited in this 7.6 eV band [17]. So, further research into the nature of the absorption at 7.6 eV in stishovite may solve some important mysteries.

However, existing similarities allow consideration that oxygen deficiency in silica glass and radiation-induced amorphization of α-quartz crystals produce defects which are similar to defects in octahedrally structured stishovite crystals.

Acknowledgments

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