

# ENERGY TRANSPORT IN $\text{SiO}_2$ CRYSTALS: LUMINESCENCE EXCITATION SPECTRA OF STISHOVITE AND $\alpha$ -QUARTZ

A. N. Trukhin

Institute of Solid State Physics, University of Latvia,  
8 Kengaraga Str., Riga, LV-1063, LATVIA  
E-mail: truhins@cfi.lu.lv

The migration of elementary electronic excitations was studied in a single crystal of stishovite and compared with migration in a crystal of  $\alpha$ -quartz and polycrystalline stishovite powder. The research method is based on comparing the transfer of absorbed energy to luminescence centers, used as detectors of quasiparticles, and the near-surface nonradiative annihilation of electronic excitations. A sign of migration is the appearance of some minima in the photoluminescence (PLE) excitation spectrum in the region of maxima in the intrinsic absorption spectrum. The PLE spectrum of stishovite contains the first minimum at 9.8 eV, indicating the migration of electronic excitations and the existence of an intrinsic absorption band in stishovite at 9.8 eV. In  $\alpha$ -quartz, the first minimum in the PLE spectrum is located at 10.5 eV and corresponds well to the intrinsic absorption band of the exciton.

**Keywords:** Electronic excitations migration, photoluminescence excitation, stishovite single crystal.

## 1. INTRODUCTION

The method for studying energy migration is based on the transfer of energy absorbed by the material to the luminescence center by the corresponding elementary electronic excitations created by the exciting light. The effect of modulating the transmission efficiency of the penetra-

tion depth of the exciting light due to the different absorption levels in the intrinsic spectrum of the material is used as a sign of energy migration. (See for example [1]–[3]). If moving elementary electronic excitations (which are the same as quasiparticles) are created in the material by

light, then their number approaching the luminescence center, which plays the role of a quasiparticle detector, depends on the competitive process of diffusion of quasiparticles into the near-surface region, where they annihilate nonradiatively. The thinner the absorbing layers, for high values of the absorption coefficient, the less the number of particles reaches the luminescence center, which is evident from the decrease in the luminescence quantum yield. Thus, at the maximum of the absorption band, a minimum luminescence yield is observed if the quasiparticles are mobile. Relationship between the yield of luminescence excited by the transfer of electronic excitations and the absorption coefficient [1] is given by:

$$\eta = K \cdot h\nu \cdot (1 + \alpha L)^{-1}, \quad (1)$$

where  $\alpha$  is the absorption coefficient,  $h\nu$  is the photon energy,  $K$  is a constant,  $L = (D\tau)^{1/2}$  is the diffusion length,  $D$  is the diffusion coefficient, and  $\tau$  is the quasiparticle life time.

The energy transfer spectra of the  $\alpha$ -quartz [3], [4] are in good agreement with expression (1) in comparison with the known optical absorption spectrum in the intrinsic range. For a stishovite crystal, such an absorption spectrum is not yet known, even the optical reflection spectra have not yet been measured. Measurement of the energy transfer spectra from the luminescence excitation spectra would make it possible to qualitatively understand the features of the intrinsic absorption spectrum of stishovite. For a single crystal of stishovite, such measurements have not yet been carried out due to difficulties with the small size of the available single crystals. For the case of stishovite in the form of powder, the luminescence excitation spectra are measured [5] and I would very much like to get the spectra of a single crystal.

In fact, a comparison of the optical

properties of the stishovite crystal and the  $\alpha$ -quartz crystal revealed differences in the positions of the intrinsic absorption edges. For  $\alpha$ -quartz crystal, the intrinsic absorption edge obeys the Urbach rule in the form interpreted by Toyozawa (see, e.g., [6]). This means an exponential spectral dependence with a shift towards lower energy as the temperature rises. At 293 K, the absorption coefficient is  $10 \text{ cm}^{-1}$  at 8.5 eV. At 600 K, the same absorption level occurs at 7.9 eV. For a single crystal of stishovite, the fundamental absorption edge does not depend on temperature, the level of the absorption coefficient equal to  $10 \text{ cm}^{-1}$  is at 8.75 eV [7].

Stishovite has not yet been sufficiently studied; however, theoretical and experimental approaches to the study have now begun and the first results have been obtained [7]–[10]. These publications revealed the luminescence of defects present in the grown stishovite single crystal. In a freshly grown single crystal of stishovite, two types of luminescence centers with two bands were observed. One UV (4.75 eV), the other blue (3.1 eV) [7] are observed under excitation of x-ray [8], e-beam [9] and excimer lasers [10]. The process of luminescence excitation is complex. One part of the process is associated with intra-center excitation of the defect. In this case, a rapid decay of photoluminescence is observed, amounting to  $\sim 17 \mu\text{s}$  for the blue band and 1–2 ns for the UV band at 80 K [11]. Another part of the process is recombination. Thus, the effect of increasing the photoluminescence duration up to ms for the blue band and up to tens of microseconds for the UV band was discovered when a single crystal of stishovite was heated even to a high (340 K) temperature [12]. The effect is explained by the formation of a certain complex with an OH group or / and a diamond-like carbon defect upon photo-

excitation of the luminescence center. The complex is destroyed by heating, providing slow recombination luminescence [12].

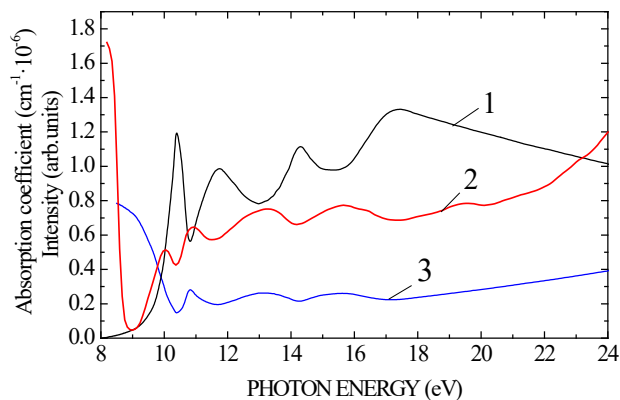
The small size of the stishovite single crystal made it difficult to observe the photoluminescence upon excitation with conventional discharge light sources. An attempt was made to measure the luminescence excitation spectra of a stishovite single crystal using a windowless light source with a discharge in hydrogen through a vacuum monochromator. The main measurement method was the use of the opti-

cal transparency of a stishovite single crystal. The sample was pressed into a copper holder with a hole sealed with indium. The holder also served as a shield against scattered light from the monochromator, and the glow was recorded on the other side of the excited sample. In addition to collecting light with a concave mirror, a long integration of the measuring point was carried out. The measurements were taken through a blue filter.

## 2. ENERGY TRANSPORT IN QUARTZ

Energy transfer spectra for an  $\alpha$ -quartz crystal have been measured over a wide

range of photon energies [4], [13].



*Fig. 1.* The absorption spectrum of crystalline quartz – 1 calculated using  $k$  [13] ( $\alpha=2\pi k/\lambda$ , where coefficient  $k$  – extinction and  $\lambda$  is wavelength) and the luminescence excitation spectrum of  $\text{Cu}^+$  centers – 2,  $T = 290$  K. Also, the energy transfer spectrum calculated according to expression (1) – 3, which was calculated under the condition of one type of migrating quasiparticle (only one value is assumed  $L = (D\tau)^{1/2} - 100$  nm). The observed difference with the measured PLE spectrum is explained by the fact that energy transfer is carried out by many different electronic excitations [4], [14]. The point 8.5 eV is a boundary separating intrinsic absorption and intracenter absorption in quartz.

As the main effect, it was found that the luminescence excitation spectra corresponded to expression (1) when compared with the known optical absorption spectrum in the intrinsic range (Fig. 1). Here, the intrinsic absorption maxima (represented

by the reflectance spectrum) correspond to minima in the measured luminescence excitation spectrum, indicating the transfer of absorbed energy. Details of interpretation can be found in [14].

### 3. ENERGY TRANSPORT IN STISHOVITE

The measurements of luminescence excitation spectra for stishovite single crystal

were performed through blue filter.

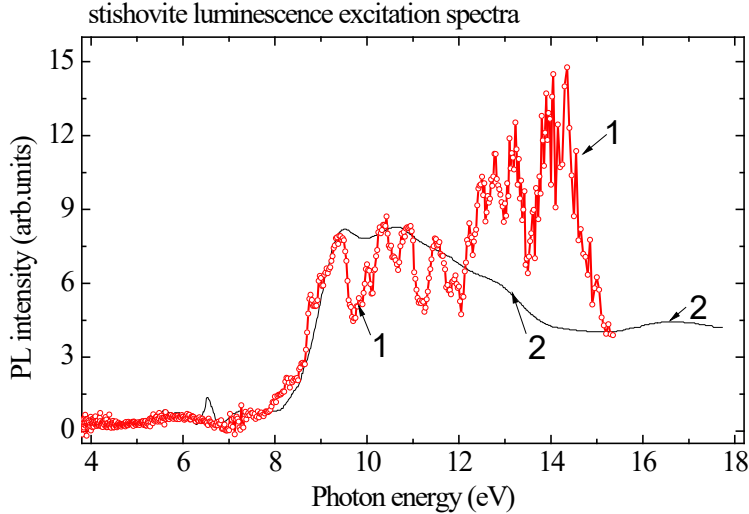


Fig. 2. Photoluminescence excitation spectra of stishovite single crystal – 1 (points connected with a line to guide eye) and spectrum of stishovite powder – 2 taken from paper [5]. The points in 1 above 12 eV are noisier because of smaller light intensity of hydrogen discharge light source in this range of spectrum.

The best result is shown in Fig. 2. There is a good agreement between the PLE spectra of a single crystal and the previously measured PLE spectra of stishovite powder [5] using radiation from a storage ring. The first minimum at 9.8 eV is present in both spectra, although in the spectrum of Ref. [5] the modulation is not so expressive. This can be explained by the migration of energy, which is better in a single crystal than in powder.

I did not consider other minima in the PLE spectrum (for example, at 10.6 and 11.9 eV), because there is no correlation with the spectrum from [5], apparently measured with much greater accuracy. Thus, we can assume the presence of a band at 9.8 eV in the intrinsic absorption spectrum of stishovite. The predicted band at 9.8 eV is

possibly some analogue of the 10.5 eV band in  $\alpha$ -quartz. However, there is still no evidence of the exciton nature of the 9.8 eV band. Other minima in the noisy spectrum measured by me require additional verification.

The mechanism of energy migration in stishovite is assumed to be realized by electron-hole pairs, since we did not find signs of excitons, for example, due to the lack of observation of a self-trapped exciton. If excitons could be created by light in stishovite, they effectively dissociated into electron-hole pairs. This is in contrast to  $\alpha$ -quartz, where electron-hole pairs created by light have a short lifetime [15], effectively compressing to excitons, thereby providing a very efficient creation of self-trapped excitons.

## 4. CONCLUSIONS

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The energy absorbed by a single crystal of stishovite leads to the creation of quasiparticles – electron-hole pairs, which migrate in the volume and excite defects, which are detectors of electronic excitations. The measured emission spectrum of

the detectors indicates the presence of some bands in the intrinsic absorption spectrum. The intrinsic absorption band at 9.8 eV is most clearly revealed experimentally.

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