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Nanosecond Duration Broadband Luminescence of Quartz Glasses

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Abstract

The results of investigations of luminescence, excited by radiations of N_2 - and Nd^{3+} : YAG-lasers ($\lambda = 337nm, \lambda = 532nm$) in high purity quartz glasses are reported. The luminescence has broad spectrum (350-850 nm) and very short duration (1-20 ns).

1. Introduction

Absorption spectrum of transparent substances is composed of three parts (Figure 1) [1]: part A corresponds to band-to-band transitions; part B is called an edge of the fundamental absorption and described by the following relationship (Urbach's rule) [2]:

$$\alpha = \alpha_0 \exp[\sigma(\hbar\omega - \hbar\omega_0)/kT].$$

The parameter σ , indicating an exponent steepness, depends on the temperature; α_0 and $\hbar\omega_0$ are constant values. Some authors [3] consider the appearance of part B to be the result of a direct creation of an autolocalized exciton, and other authors [4] consider it as a transition of an exciton on a Stark broadened excited state. Part C corresponds to a transparency region for the substance. The absorption coefficient in this region is also described by an exponential relationship, as in Urbach's rule, but with a different index. Most investigators connect the light absorption in this region with the small, uncontrolled amount of impurities in the substance [1]. However, the mechanism of this absorption and why it is described by universal relationship, as in region B, among other questions, remain practically uninvestigated up until now.

Quartz glasses with 9-10 eV energy gap have several absorption bands (AB) and corresponding to them luminescence bands (LB) in the near UV and visible region of spectrum, depending on the type of glasses. Absorption spectra of Type III and Type IV quartz glasses are similar to region C in the 200-800 nm, where their absorption coefficients monotonically decrease with increasing wavelength and noticeable AB are not observed. The one exception is that the broadband absorption spectrum in Type I and Type II quartz glasses AB at 242 nm is observed as well. This AB is connected with germanium impurity in the SiO_2 . The luminescence excited in the AB at 242 nm has two bands: the first at 280 nm, and the second at 400 nm [5]. By analysing the absorption spectrum of quartz glasses we can say that region of spectrum, beginning from 180 nm, is concerned with region C [6]. In this region other AB and LB, except the AB at 242 nm and the corresponding LB at 280 nm and 400 nm, are not observed in the unirradiated and unactivated samples of quartz glasses.

Unknown earlier, fast broadband luminescence (FBL) of quartz and multicomponent glasses, excited by N_2 -laser radiation ($\lambda = 337nm$), was recently observed [7, 8]. With the wavelength of exciting light lying in region C, one can investigate properties of FBL and obtain new information about processes taking place in the transparency region of materials. FBL, having a very broadband spectrum (from exciting wavelength to 850 nm) and very short duration (1-20 ns), essentially differs from known LB of quartz glass. Spectral and kinetic properties of FBL are changing under influence of γ -radiation and temperature [8, 9]. This letter is a continuation of investigations of FBL properties and devoted to the study of its spectral and kinetic characteristics with increasing excitation wavelength in different types of quartz glasses.

2. Experiment

Quartz glasses KI (Type I), KU-2 and KV (Type II), KU-1 (Type III) and KUVI (Type IV) were used in experiments. Absorption spectra were measured on spectrophotometer Specord-UV-VIS. Luminescence spectra were recorded at right angle to direction of the excitation light by using a strobe method. There were possibilities to change the width of measuring strobe from $200 \times 10^{-12}s$ up to $400 \times 10^{-6}s$ and its relative position to the peak of the luminescence pulse. The experimental setup included: MDR-23 monochromator with diffraction grating; FEU-77, FEU-79 high sensitivity photomultipliers and boxcarintegrator BCI-280. Time characteristics of luminescence were investigated by using strobe method as well. In these experiments, width of measuring strobe was equal to $200 \times 10^{-12}s$ and duration of luminescence was determined between the half heights of the measured pulse. Luminescence was excited by N_2 -laser radiation ($\lambda = 337nm, \tau \sim 9ns, P \sim 10kW$) and the second harmonic of a Nd^{3+} : YAG-laser ($\lambda = 532nm, \tau \sim 30ns, P \sim 500kW$). Setup was controlled by the computer.

3. Results and Discussion

In Figure 2 absorption spectra of investigated samples are presented. As seen in these spectra, asside from the one AB at 242 nm, other absorption bands are not observed. Estimating absorbtion coefficients at wavelengths $\lambda = 337nm$ and $\lambda = 532nm$ gives values of $\sim 10^{-3}cm^{-1}$ and $\sim 10^{-4}cm^{-1}$ respectively. In Figure 3, luminescence spectra of these samples are presented (excitation wavelength $\lambda = 337nm$, width of strobe equal to 40 ns, measuring strobe cover peak of luminescence pulse). Luminescence spectrum of KU-2 glass is similar to KV glass, but there is strong difference between their intensities. FBL duration in KU-1 and KUVI glasses is no more than 9 ns, that is luminescence pulse repeats shape of the excitation pulse. In KI, KU-2 and KV glasses FBL duration is about 20 ns. As seen from Figure 3, the half width of FBL spectrum increases with increasing sample purity. Four types of quartz glasses differ from one another not only in manufacturing technology, but also in concentration of different metallic impurities and OH-groups [10]:

- Type I: metallic ions $\sim 10^{-2}wt.%$, OH-groups $< 5 \times 10^{-4}wt.%$;
- Type II: metallic ions $< 10^{-2}wt.%$, OH-groups $\sim 2 - 6 \times 10^{-2}wt.%$;
- Type III: metallic ions $< 10^{-4}wt.%$ OH-groups $\sim 0.2wt.%$;
- Type IV: metallic ions $< 10^{-4}wt.%$, OH-groups $\leq 10^{-3}wt.%$.

In the same conditions of excitations and measurements of luminescence the smallest luminescence intensity is observed in glass KU-1. If we compare integrated intensities of FBL of different samples to KU-1 (considering integrated intensities of FBL of KU-1 as unit), then we have following values of integrated intensities of FBL in different types of quartz glasses: for KU-2, ~ 10 ; for KV, ~ 30 ; for KI, ~ 150 .

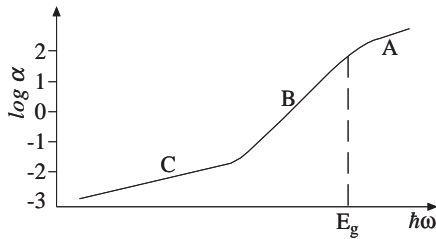


Figure 1. Absorption spectrum of transparent substances: Part A corresponds to band to band transitions, Part B - Urbach's edge, Part C - a transparency region of substance. E_g - the width of energy gap

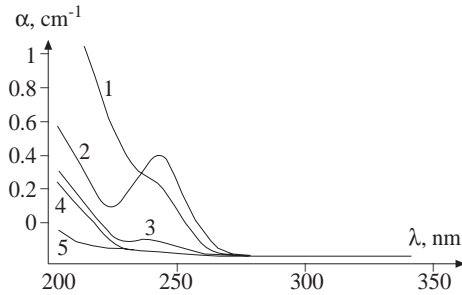


Figure 2. Absorption spectra of quartz glasses: 1 - KI, 2 - KV, 3 - KU-2, 4 - KU-1, 5 - KUVI

The least intense FBL is observed in KU-1 quartz glass under excitation with radiation in the green range. In Figure 4, luminescence spectra of FBL excited by second

harmonic of Nd^{3+} : YAG-laser radiation ($\lambda = 532nm$) are presented. One can consider the spectra as a superposition of two bands with maxima at 750 nm and in the region of 600 nm. Determination of the value of spectral maximum about 600 nm is a difficult task because of the effect of Raman scattering at 1200 cm^{-1} . If in region 600-800 nm we compare integrated intensities of FBL with one another as in the case of excitation in UV region ($\lambda = 337nm$), then we have such values: KU-1, ~ 1 ; KU-2, ~ 1.1 ; KI, ~ 1.2 .

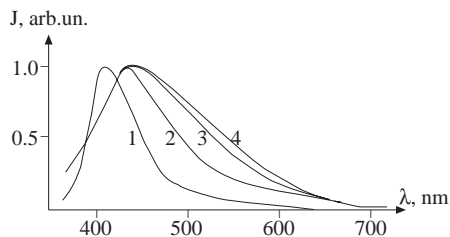


Figure 3. Luminescence spectra of investigated samples excited by radiation of N_2 -laser ($\lambda = 337nm$): 1 - KI, 2 - KV, 3 - KUVI, 4 - KU-1. Spectra are normalized independently, width of strobe is 40 ns

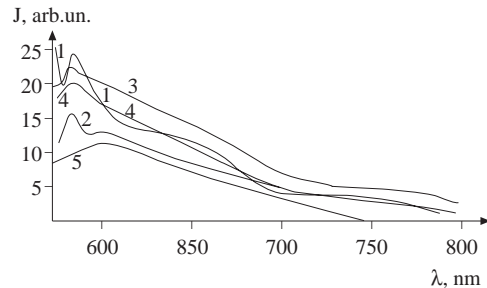


Figure 4. Time-resolved luminescence spectra of quartz glasses, excited by radiation of Nd^{3+} : YAG-laser ($\lambda = 532nm$): 1 - KU-2, 2 - KU-1, 3 - KUVI, 4 - KI (strobe cover peak of luminescence pulse), 5 - KI (delay time of strobe is 60 ns relatively to beginning of luminescence pulse). Spectra are normalized independently, width of strobe is 40 ns

The pulse full-width at half maximum duration of luminescence is no more than the width of the excitation pulse, that is 30 ns. However, luminescence pulse in Type I and Type II quartz glasses contains a very weak, relatively "slow" component. In Figure 4 (curve 5) time-resolved spectrum of FBL of glass KI is presented. This spectrum was received when measuring strobe with width of 40 ns had delay time of 60 ns relative to the beginning of the luminescence pulse. As seen, in the spectrum the Raman scattering band is absent and spectral maximum of luminescence is found at 610 nm. But one cannot say anything about the band at 750 nm because of a very small intensity of luminescence in this region. The occurrence of time-resolved spectra show that the luminescence duration in KI is more than that of the excitation light duration, and luminescences in quartz glasses excited by wavelength of 532 nm and 337 nm have a single feature.

In [8] a model of absorption and FBL centers in silica glasses in the form $\equiv Si - O \cdots +M \cdots Si \equiv$ (M -center) has been proposed, where $+M$ is an impurity ion incorporated into the glass network during the formation process. It is supposed that absorption and luminescence in this model take place in the fragment $O^- \cdots +M$. Such centers could be formed in the time of glass cooling and/or after exposition by

high energy radiation. In addition, the valence - alternation pairs (VAP's) could also be their precursors. VAP's - positive charged three-coordinated Si_3^+ (or O_3^+) and negative charged non-bridging oxygen O_1^- - are produced and frozen by breaking a $Si-O$ band in the network [11-13]. VAP's give rise to two levels in the energy gap of SiO_2 ; the first level (O_1^-) is near the valence band and the second level (Si_3^+) is near the conduction band [13]. The existence of such point defects has not been proved directly and some authors call them in question [5, 14]. VAP's are intrinsic defects of SiO_2 and must exist in all types of quartz glasses and their absorption and luminescence characteristics do not depend on the impurity concentration. The presence of the impurities near the VAP's may leads to interaction with Si_3^+ (or O_3^+) and form M -centers, their energy levels between the O_1^- and Si_3^+ levels (Figure 5). Possibility of excitation of FBL in the different parts of the spectrum and its broad spectrum are due to a variety of impurity atoms and their special nonequivalent positions in the glass network. One must take into account that not all impurity atoms in the structure of SiO_2 give rise to optically active centers. Especially OH - groups and hydrogen do not create optically active centres in the UV and visible parts of spectrum and can modify existing color centres [15]. It is possible, that the least FBL intensity in KU-1 is connected not only with small metallic impurity concentration, but also with high concentration of OH-groups.

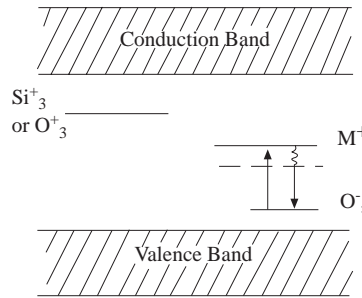


Figure 5. Scheme of energy level arrangements for states associated with Si_3^+ (or O_3^+), O_1^- and M^+ -center

More differences in FBL intensities in different types of quartz glasses excited by N_2 -laser radiation ($\lambda = 337nm$) than that excited by Nd^{3+} : YAG-laser radiation ($\lambda = 532nm$) are connected, probably, with Ge impurity, existing in Type I and Type II quartz glasses in very small concentration. The germanium impurity gives rise to AB at 330 nm [16]. This AB is very weak and does not discriminate the absorption spectrum of quartz glass, which monotonically reduces with increasing wavelength. Excitation at 330 nm produces LB with spectral maximum at 400 nm and decay time of about $100 \cdot 10^{-6}s$ [17]. This microsecond luminescence emission spectrum of impurity Ge , which does not take part in forming the M -centers, may be detected in Type I and Type II quartz glasses by time-resolved method, the delay time of measuring strobe from luminescence pulse peak being equal to a few microseconds.

Thus, it may be concluded that fast broadband luminescence is excited in all quartz glasses both in UV and in visible region of spectrum. Excitation efficiency of FBL in optical glasses is decreased with the increasing of the excitation wavelength that is confirmed by decreasing of absorption coefficient in part C. The luminescence intensity is changed not only from type to type of quartz glasses, but also within the series of the same type glasses, indicating the significance of glass synthesis condition. FBL duration is not more than 30 ns in spectral range 600-800 nm, but it changes from 1 ns to 20 ns in the range 350-600 nm. At present, FBL may be explained qualitatively by radiation of M -centers, being formed of quasi-molecular complexes: $\equiv Si-O^- \cdots ^+M \cdots Si \equiv$. Valence-alternation pairs could be precursors of these centres, which are formed by interactions of impurities and VAP's.

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