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BRIEF MESSAGE

Luminescence of Oxygen-Deficient Centers in Quartz Glasses

T. Yu. Garmysheva[a], *, R. Yu. Shendrik[a], A. S. Paklin[a], A. A. Shalaev[a], E. V. Kaneva[a], and A. I. Nepomnyashchikh[a]

[a] *Vinogradov Institute of Geochemistry, Siberian Branch, Russian Academy of Sciences, Irkutsk, 664033 Russia*
**e-mail: tatyanasiz85@yandex.ru*

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Abstract—This paper presents the results of studying the absorption, luminescence, and excitation spectra of oxygen-deficient centers (ODCs) in glasses obtained from quartz raw materials with different contents of the cristobalite phase (0–80%). With an increase in the content of the cristobalite phase, an increase in the intensity of the luminescence band corresponding to singlet-singlet transitions in the center of the oxygen vacancy type near the germanium impurity ion is observed. Differences in the short-range order of quartz glasses obtained from the initial raw materials with different contents of α-quartz and cristobalite phases are studied.

Keywords: quartz glass, α-quartz, cristobalite, luminescence

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INTRODUCTION

High-purity and germanium-doped quartz glasses used in the manufacture of optical fibers are characterized by absorption bands of silicon and germanium oxygen-deficient centers (ODCs) with the maximum of about 240 nm [1]. The presence of these defects significantly affects the electrical, optical, and luminescent properties of quartz glass. Nominally pure quartz glasses, when excited in the 240-nm region, have luminescence bands with maximums in the region of 280 and 460 nm, while in glasses doped with germanium, luminescence is observed at 292 and 396 nm. These photoluminescence bands are attributed to singlet and triplet radiative transitions in the ODC(II) and Ge-ODC(II) (germanium oxygen deficient center), respectively [2].

As a result of a comprehensive study using X-ray phase diffraction (XRD) analysis, as well as optical and electron probe microscopy [3], it was found that quartz glass samples obtained from cristobalite grains are more resistant to crystallization than glasses obtained from alpha-quartz grains. A possible reason for this effect is the difference in the short-range order in these glasses, which should manifest itself in the luminescence properties.

This paper presents the results of studies of the luminescence of ODCs in quartz glasses obtained from natural quartz of various modifications: α-quartz and cristobalite.

EXPERIMENTAL

The quartz glasses studied in this paper were obtained from high-purity quartzites from the Bural-Sardyk deposit [4]. The original natural quartz consists of grains with the average size of 100 μm. According to the results of infrared spectroscopy (IR), as well as the results of analysis by inductively coupled plasma mass spectrometry (ICP MS), the quartz grains used in the experiments after chemical enrichment contain no more than 10 ppm impurities [3]. In this paper, we studied the photoluminescence and absorption spectra of glasses obtained from α-quartz grains and glasses obtained from quartz grains with different contents of the cristobalite phase in the initial charge (0–80%). The cristobalite phase is formed after calcining the grains at a temperature of 1450°C for 24–48 h. The phase content of α-quartz and cristobalite in grains were controlled by XRD. Glasses were fabricated on a modernized plant for growing OKB-8093 single crystals by vacuum-compression melting at the maximum pressure of up to 6 bar [5].

The absorption spectra of transparent polished plane-parallel quartz glass plates 1.5 mm thick were measured on a Perkin Elmer Lambda 950 double-beam spectrophotometer.

The photoluminescence and excitation spectra were measured on a Perkin Elmer LS-55 spectrofluorimeter.

RESULTS AND DISCUSSION

The absorption spectrum of all glasses studied at room temperature exhibits a band with the maximum

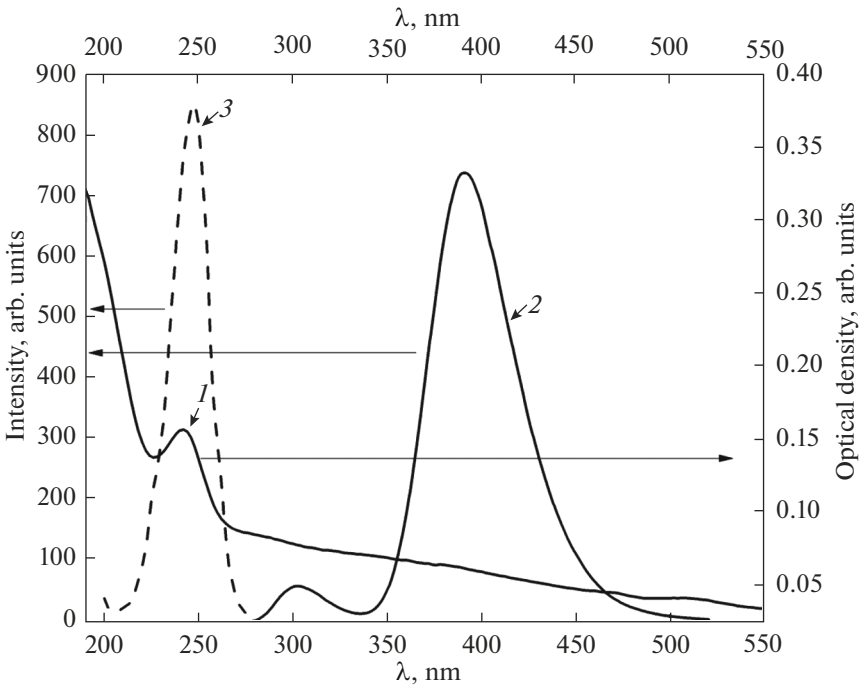

Fig. 1. Absorption spectra (*1*), photoluminescence (*2*) ($\lambda_{excitation}$, 240 nm) and excitation (*3*) (λ_{lum}, 302 nm) of quartz glass, measured at room temperature.

in the region of 240 nm (Fig. 1). This absorption band is due to defects of the oxygen vacancy type near the Ge impurity (Ge-ODC(II)) [1, 2]. A similar absorption band is observed in pure glassy GeO_2 [6]. In the photoluminescence spectra of glasses obtained from α-quartz and glasses obtained from quartz raw materials with a low content of the cristobalite phase (up to 30%), two bands are observed in the region of 390 and 302 nm.

The luminescence band at 390 nm is related to the triplet–singlet (T_1–S_0) transition, and the high-energy band with the maximum at 302 nm is related to the singlet–singlet transition (S_1–S_0) in centers of the oxygen vacancy type near the germanium impurity in quartz glass (Ge-ODC(II)) [1, 7, 8]. In the absorption and excitation spectrum, the band at 240 nm is related to the singlet–singlet transition from the ground state $1A_1$ (S_0) to the excited singlet state B_2 (S_1) [1]. The appearance of such centers in the studied glasses is related to strongly reducing atmospheric conditions during their manufacture [8].

Figure 2 shows the photoluminescence spectra of quartz glasses obtained from quartz with different phase ratios of α-quartz and cristobalite in the feedstock. In the spectrum of glass obtained from α-quartz (spectrum *1*), the triplet–singlet transition band at 390 nm is the most intense. With an increase in the content of the cristobalite phase (spectrum *2*: the glass was obtained from quartz grains containing 31% of the cristobalite phase and spectrum of 3 to 76% of the cristobalite phase), an increase in the intensity of the singlet–singlet transition band of Ge-ODCs(II) at 302 nm is observed.

Figure 3 summarizes the results of a study of a group of glasses obtained from quartz grains with different ratios of the α-quartz and cristobalite phases and shows the dependence of the ratio of the triplet and singlet luminescence intensities of Ge-ODCs(II) on the content of the α-quartz phase in the feedstock.

Previously, different ratios of triplet and singlet luminescence intensities were observed in the spectra of glasses irradiated with an electron beam [9], as well as during heat treatment of glasses [10]. The observed effects are possible due to the violation of stoichiometry during irradiation, the evaporation of germanium from the glass surface, and violation of the homogeneity of the samples. In the glasses studied in this paper, the concentration of germanium in the initial raw material was the same, and Ge-ODCs(II) were created in the course of glass synthesis due to a strongly reducing atmosphere. In this case, the synthesis conditions were the same, and only the phase composition of the initial raw material from which the glass was made differed. Thus, the germanium concentration and stoichiometry in glasses are the same, and the differences in the luminescence spectra cannot be caused by these factors. In addition to differences in the ratio of the intensities of singlet and triplet luminescence, attention is drawn to the fact that the band in the excitation spectrum of glass obtained from α-quartz has the maximum at 240 nm, while the maximum of the

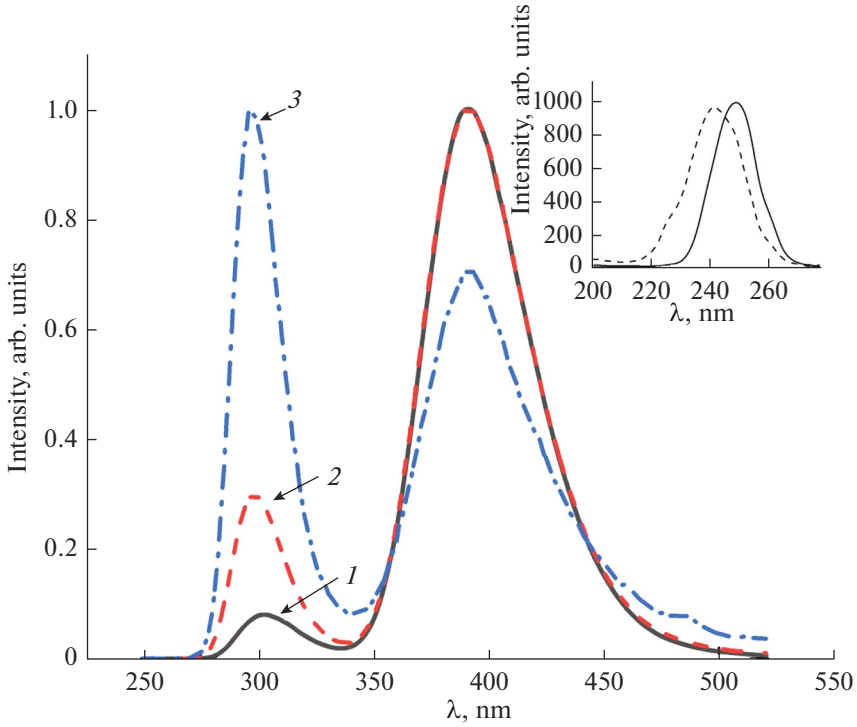

Fig. 2. Photoluminescence spectrum of quartz glass measured at room temperature. Glass obtained from α-quartz ($\lambda_{excitation}$, 240 nm) (*1*), 30% cristobalite, 70% α-quartz in the feedstock ($\lambda_{excitation}$, 240 nm) (*2*), 76% cristobalite, 24% α-quartz in the feedstock ($\lambda_{excitation}$, 248 nm) (*3*). The inset shows the excitation spectrum of glass obtained from α-quartz (solid line), glass obtained from feedstock with a high content of cristobalite (from 70%) (λ_{lum}, 302 nm).

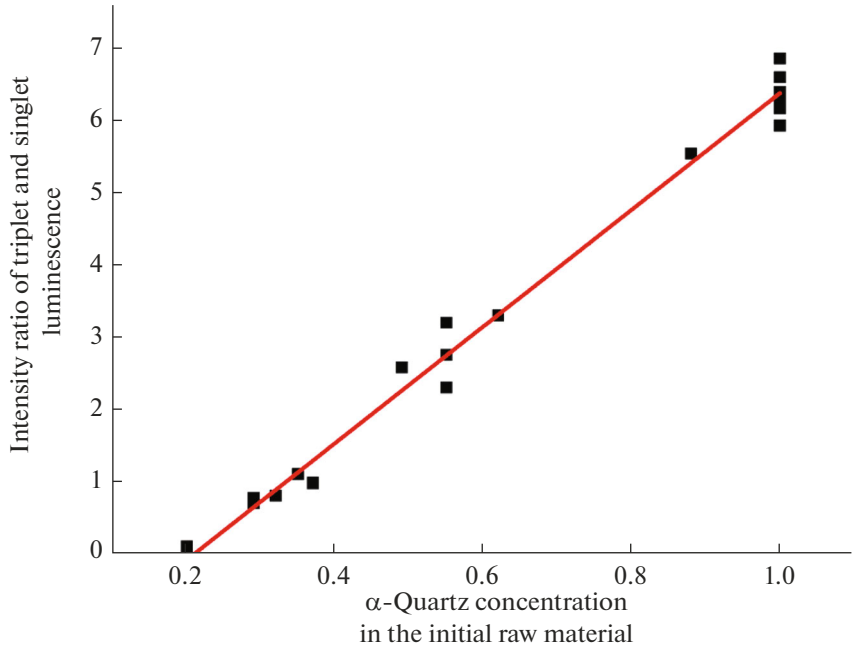

Fig. 3. Dependence of the intensity ratio of the triplet and singlet luminescence of Ge-ODCs(II) on the content of the α-quartz phase in the feedstock.

excitation band in the spectrum of glass obtained from cristobalite is shifted and lies in the region of 248 nm (inset, Fig. 3).

The luminescence of Ge-ODCs(II) was noted in [11] to be similar to the luminescence of self-trapped excitons. In crystalline α-quartz, two types of differently oriented self-trapped excitons are observed (luminescence at 2.5 eV (496 nm) and 2.7 eV (460 nm)). Differences in the excitation bands are observed in crystalline quartz and cristobalite, which is due to the difference in the geometry of the environment, and, accordingly, in the configuration of the near-impurity exciton in quartz and cristobalite.

The difference in the excitation spectra of glasses obtained from α-quartz grains and from grains with a high content of the cristobalite phase can also indicate differences in the configuration of the Ge-ODCs(II).

As a result of the studies, we can conclude that the observed differences in the intensities of singlet and triplet luminescence in quartz glasses, as well as in the excitation spectra, indicate that the short-range order in glasses obtained from quartz grains with different contents of the α-quartz phase and cristobalite, is different. In a sense, glass inherits the structure of the original charge. Moreover, the luminescence of Ge impurity centers is sensitive to the change in the short-range order of quartz glass. A similar effect was also observed in radiation-irradiated glasses in [12], where it was shown that the configuration of E' centers, determined by the EPR method, in glasses made from cristobalite and α-quartz differed significantly.

CONCLUSIONS

It was found that the ratio of singlet and triplet luminescence bands of Ge-ODCs(II) in glasses obtained from quartz concentrates depends on the ratio of the α-quartz and cristobalite phases. The intensity of the singlet band increases with an increase in the content of the cristobalite phase in the feedstock.

Based on the study of the excitation spectra of glasses made mainly from cristobalite and alpha quartz, it was found that the observed changes in the ratio of singlet and triplet luminescence are possibly related to the difference in the short-range order of the studied glasses.

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CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

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