

Luminescence of neutron-irradiated quartz crystals

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Abstract. The effect of crystal structural inhomogeneities in the form of β -phases, metamict phases, as well as point defects and impurities on the kinetics of phase transformations and amorphization occurring in quartz crystals under neutron irradiation has not been sufficiently investigated. For this reason, the kinetics of gamma-luminescence (GL) and photoluminescence (FL) bands in quartz crystals grown on seeds irradiated with neutrons at a dose of $5 \cdot 10^{18}$, 10^{19} and $5 \cdot 10^{19}$ n/cm² after additional neutron irradiation of 10^{16} - $8 \cdot 10^{20}$ n/cm² in the temperature range of 77-300 K. Based on the analysis of luminescent properties, the nature of intrinsic defects in the structure of quartz crystals, their role in the formation of color and glow centers, has been studied. Based on the analysis of experimental data, the study of the luminescent properties of quartz crystals determined the properties of various centers of luminescence and the formation of color centers of crystalline quartz.

1 Introduction

It is known that point defects of the structure are formed in quartz crystals under the action of neutrons, local centers are transformed and structural phase transformations are observed [1, 2]. The study of various physicochemical properties of neutron-irradiated crystals shows that up to doses of 10^{17} n/cm², mainly the manifestation of pre-radiation defects, impurity color centers, transformation of local centers and radiation-induced point defects of the structure is observed [3]. At higher radiation doses, the role of complexes of defects and structural transformations is manifested. The disappearance of IR absorption bands associated with the main vibrations of the α -quartz lattice [1], an increase in thermal stability some structural defects, the appearance of new IR absorption bands and luminescence [5].

2 Methods

However, Currently, there is no systematic study of radiation – optical properties, in particular, the luminescent properties of neutron-irradiated quartz crystals due to structural phase transformations, the use of a complex of theoretical and experimental research

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methods. Investigation of the mechanism of the radiation α - β transition by IR spectroscopy, gamma-luminescence (GL) and X-ray diffraction analysis has shown that the α - β transition under neutron irradiation occurs through the formation of the β -phase nuclei of quartz and the amount of β -phase increases with the dose of neutrons. It is assumed that the IR absorption bands with maxima of 3640 and 3660 cm^{-1} and the GL bands of 550 , 460 nm , respectively, are due to the β - and metamict phases of quartz (see in [1,5]).

3 Experimental results

A study of the GL of quartz crystals irradiated with doses of $10^{16} - 8 \cdot 10^{20}\text{ n/cm}^2$ neutrons in the temperature range of $77-300\text{ K}$ showed that a band of 490 nm is observed in the range of $77-200\text{ K}$. The intensity of the band in crystals irradiated with doses of 10^{18} and $5 \cdot 10^{18}\text{ n/cm}^2$ to a temperature of 150 K remains almost constant, and then a decrease is observed (Figure 1). The intensity of the 490 nm band decreases with an increase in the dose of neutron irradiation. In type (II) crystals, the intensity also decreases with an increase in the radiation dose of the seed (Figure 2).

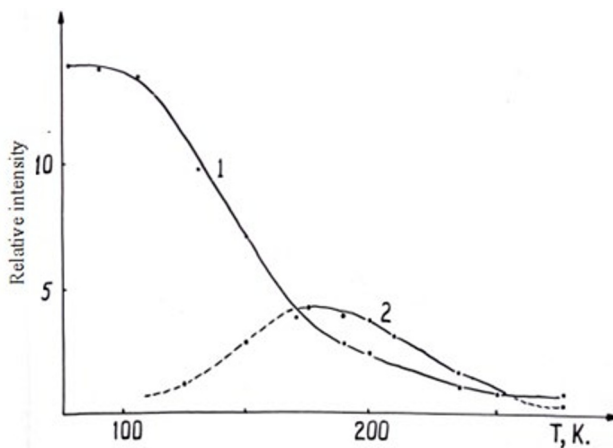


Fig. 1. Temperature dependences of bands 490 (1) and 420 nm (2) in $\text{SiO}_2:\text{AL}$.

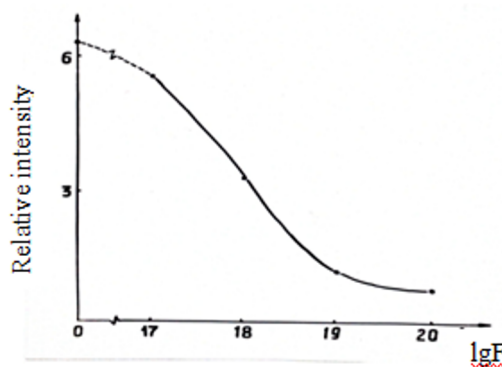


Fig. 2. Dependence of the intensity of the 490 nm band on the dose of neutron irradiation of seeds in type II crystals at 77 K .

In crystals irradiated to 10^{17} n/cm² at temperatures above 200 K, bands of GL 450 and 420 nm appear, and at doses $> 10^{17}$ n cm⁻² bands with maxima of 550 and 660 nm appear. At doses $> 10^{19}$ n/cm², a decrease in their intensities is observed.

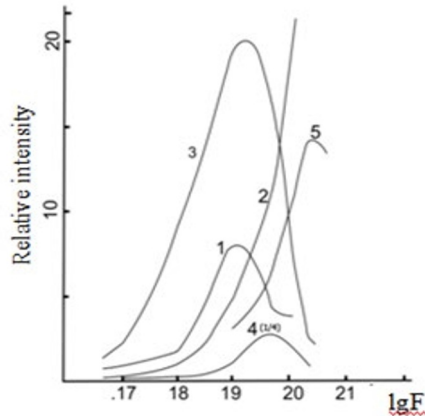


Fig. 3. Dependences of the intensities of the bands PL 550 (1), 660(2), 840 nm (4) and GL 660 (3), 460 nm (5) on the fluence of neutrons.

In crystals irradiated with a dose of $2 \cdot 10^{20}$ n/cm², the band with a maximum of 550 nm disappears and a band of 460 nm appears (Figure 3). In the case of FL, the intensity of the 660 nm band constantly increases with the neutron irradiation dose. For the first time, along with the known luminescence bands, a new band with a maximum of 840 nm was detected in the FL, GL and TL spectra. The intensity of the band increases with the dose to $5 \cdot 10^{19}$ n/cm², and then decreases (Figure 3). At doses of 10^{20} n/cm², the band disappears. The study of the dependence of the intensity of the band on the excitation temperature of the GL shows that an increase in its intensity is observed in the 77–120 K region. At 130 K, its intensity decreases sharply and remains almost constant in the future (Figure 4).

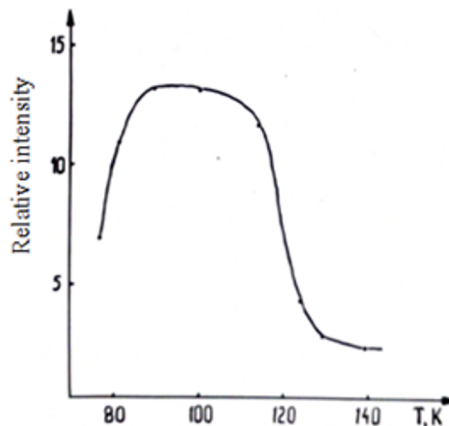


Fig. 4. Dependence of the intensity of the 840 nm band on the excitation temperature.

At doses of 10^{20} n/cm², the band disappears. The study of the dependence of the intensity of the band on the excitation temperature of the GL shows that an increase in its intensity is observed in the 77–120 K region. At 130 K, its intensity decreases sharply and remains almost constant in the future (Figure 4).

4 Discussion of the results

It was assumed that the 490 nm band is caused by the glow of autolocalized exciton (ALE) formed by recombination. The authors of [7] suggest that the X-ray luminescence bands observed in the temperature range of 80-800 K arise due to the recombination of electrons with holes captured from various aluminum-oxygen tetrahedra. Electron paramagnetic resonance (EPR) studies have shown that crystals irradiated at temperatures <145 K form $(\text{Al O}_4)^0$ centers, and atomic hydrogen H_0 [8]. It is assumed that in this case the decay (AlO_4) occurs H-center due to the withdrawal of hydrogen. If the temperature of the sample irradiated at 77 K rises to 130 K, then there is a thermal release of electrons from the capture levels formed by hydrogen, and a sharp decrease in the number of $(\text{AlO}_4)^0$ – centers. This shows that in the 77–200 K region, (Al O_4) can enter as glow centers Me^+ - centers [7]. At temperatures ≥ 200 K, due to radiation-stimulated diffusion, metal withdrawal is observed and it is transformed into a hole (Al O_4) center (I and II).

To clarify the possible role of hole (AlO_4) centers to act as centers of luminescence of the 490 nm band, GL nominally pure, natural and artificial crystals with an admixture of Al were studied [11]. At the same time, crystals with an admixture of Al were irradiated to saturation of the smoky color at 77 and 300 K, and then at a temperature of 77 K, the spectra of GL were taken. The study showed that at the same time the intensity of the 490 nm band decreases. This shows that the centers of the smoky color are not the centers of the glow of the 490 nm band. It should be noted that an absorption band with a maximum of ~ 460 -490 nm (I) is observed in gamma-irradiated crystals, and a decrease in the intensity of the voice of GL 490 nm occurs, apparently, due to the reabsorption of the glow. In order to clarify the possible role of $(\text{AlO}_4)^0$ -centers formed due to the destruction of $(\text{AlO}_4)\text{H}$ -centers were studied for the GL of crystals exposed to electrical treatment (EO) in air at high temperatures, where the number of (AlO_4/H) -centers is obviously much greater than in untreated crystals [1]. Comparison of the intensities of 490 nm bands in untreated crystals at 77 K showed that after processing, the intensity increases by about an order of magnitude. However, the study of IR absorption spectra did not allow us to establish a correlation between the change in the intensities of the 3385 cm^{-1} band due to the $(\text{AlO}_4)\text{H}$ -center (I) and the 490 nm band. It was found that in nominally pure crystals, the intensity of the 490 nm band is greater than in other impurity crystals. The above data allow us to state unequivocally that the 490 nm band is its own and does not arise due to the recombination of an electron with a hole captured by the (AlO_4) center [7]. Then, taking the model of the glow center proposed in [7] as a basis, the experimental results obtained can be explained as follows. It is known that in coloring crystals there are various traps for holes formed mainly in impurity atoms and having different activation energies (I).

During gamma irradiation, unrelaxed holes are formed in quartz crystals, which are mobile in a wide temperature range. In the process of irradiation, there is competition between two processes - the capture of unrelaxed holes by activators and glow centers. An increase in the amount of impurity leads to an increase in the probability of capturing holes by them, causes a drop in the intensity of the 490 nm band. The decrease in the intensity of the 490 nm band at gamma and neutron irradiation with the radiation dose is also apparently due to;

- a) the obstacle of radiation-induced defects to the approach of holes to the center of the glow;
- b) reducing the probability of capturing holes by the glow centers due to their destruction or transformation.

When studying the dependence of the intensity of the 490 nm band on the dose of pulsed electrons with a duration of 20 ns after irradiation after 2 ms, saturation of the intensity of the bands was detected. Based on this, it is assumed that the 490 nm band is not its own and

is associated with impurities or pre-radiation defects. According to the authors [8], the glow of autolocalized excitons causes a band with a maximum of 440 nm. Earlier in [9], it was assumed that the 477 nm luminescence band is due to recombination of an autolocalized exciton. To find out which of these bands is the glow of ALE, further research is necessary. To clarify the nature of the 420 nm band, the GL at 200 K of ordinary nominally pure, artificial and natural crystals with an admixture of Al, Ge, Fe were studied. At the same time, a glow band of 420 nm was also detected in crystals with an admixture of Al above 200 K (Figure 1). It should be noted that annealing of gamma-irradiated crystals at 300°C leads to the restoration of the glow centers of the 420 nm band.

At present, the nature of the luminescence band in the region of 420-430 nm has not been established. In [7], a 430 nm RL band was found and it is assumed that it arises due to the recombination of electrons with a hole trapped at the (AlO₄) center. Studies of the X-ray luminescence (RL) of nominally pure quartz in the range of 80-300 K also showed that along with the bands of 380 and 440 nm, a band with a maximum of ~425 nm is observed [9.10]. The 425 nm band is thermally extinguished in the 170-210 K region. According to the authors, the 425 nm band does not occur due to electron-hole recombination near aluminum ions.

In [10], when studying the low-temperature photoluminescence of natural crystalline quartz excited by photons with an energy above 6 eV (~210 nm), a wide band with a maximum of about 3 eV (~413 nm) was found. It is assumed that the luminescence centers are not associated with aluminum, which is in a tetrahedral position. The glow centers contain an admixture of aluminum, alkaline ions (metals), protons and possibly their own defects. In [1] it is assumed that the admixture of Al in association with oxygen vacancies does not form a smoky color center. The comparison shows that the characteristics of the luminescence centers of the 413 nm band are close to the characteristics of the F-centers in the additively colored leucosapfyr [1]. It is possible that the entry of Al into SiO₂ causes the appearance of a defect whose structure is similar to that of the F-center in Al₂O₃. The difference in temperature dependence, the decay time of the F-centers [8] and the centers of the 413 nm band [10], apparently, is due to the entry of compensator ions into the structure of the glow centers in quartz crystals. The study of the dependence of TL on Al concentration shows that the intensity of TL is not proportional to the density of the smoky color. In [10], when studying smoky quartz having a transparent core and a smoky face, it was found that the intensity of the 413 nm band is significantly greater in the transparent part of the crystal. The concentration of Al in the transparent region is much higher than in the smoky part of quartz.

Our comparative studies show that the intensity of the 420 nm band in non-staining and staining crystals is approximately the same. The appearance of a band at >200 K, when according to (II), radiation – stimulated diffusion of alkali metal ions is possible, indicates that there are alkali metal ions in the composition of the glow center. The disappearance of the 420 nm band after gamma irradiation with a dose of 5*10⁶ R and its recovery after annealing at 300°C also shows that there are alkaline ions in the composition of the center of the glow of the band. In [1,3], the EPR method showed that in neutron-irradiated crystals, the number of hole (AlO₄) centers increases to doses of 5*10¹⁶ n/cm² and then decreases. Based on this, it can be assumed that the disappearance of the 420 nm band in neutron-irradiated crystals at 10¹⁷ n/cm² is due either to the destruction or transformation of the centers of luminescence of the 420 nm band.

In [6], X-ray diffraction analysis showed that the amount of β-phase in neutron-irradiated crystals increases with the dose of neutron irradiation. The study of the structure of quartz crystals grown on neutron-irradiated seedings also showed that the radiation-induced β-phase is inherited by an overgrown layer and its concentration increases with an increase in the radiation dose of the seed. A band of 550 nm was detected in the GL spectra of these crystals. Based on the above data, we believe that an increase in the intensity of the 550 nm

band in crystals grown on neutron-irradiated seeds with a dose of additional neutron irradiation is due to an increase in the concentration of the β -phase. The interaction between the beta-phase embryos causes a drop in its intensity after a dose of 10^{19} n/cm². The disappearance of the 550 nm band and the appearance at $2 \cdot 10^{20}$ n/cm² of the 460 nm band caused by the metamict phase of quartz [11] is in good agreement with the fact that the transition to the metamict phase goes through the β -phases and ends at $2 \cdot 10^{20}$ n/cm². In [8], it was assumed that the centers of luminescence of the 660 nm band are non-bridge oxygen atoms and they stably exist only in the glassy state of quartz. The intensity of the 660 nm band increases with an increase in the neutron irradiation dose and a plateau is observed in the region of (4-6) $\cdot 10^{19}$ n/cm² [8]. Currently, the dominant opinion is that the amorphization of quartz crystals occurs due to the accumulation of disordered regions having sizes of 10-20 angstroms [12]. It is assumed that disordered regions have a glassy structure and the observed interaction of nuclei at certain doses of neutron irradiation leads to a decrease in their number.

Then, based on the results of [8,13], it can be assumed that up to a certain dose, the intensity of the 660 nm band should increase, and then decrease. As can be seen from Fig.3, in the case of GL, a similar dependence of the band intensity on the neutron dose is observed. In the case of FL, the results of our studies, as well as in [8], show that the intensity of the 660 nm band increases with the dose of neutrons. The plateau in the dose range (4-6) of 10^{19} n/cm² observed in [8] was not detected by us. The decrease in the intensity of the GL 660 nm band after 10^{19} n/cm² is apparently due to a decrease in the probability of excitation of the glow centers due to the appearance of the 460 nm band (Figure 3).

It should be noted that earlier in [8] a band of 660 nm in quartz crystals was observed at $\geq 10^{19}$ n/cm². Our results show that the 660 nm band in the PL and GL spectra is also observed at doses of 10^{19} n/cm², when the effects of neutrons and gamma rays are similar, i.e. when amorphization in crystalline quartz is practically absent. The comparison shows that the maxima of the excitation bands of the 660 nm luminescence band in quartz glass ($\lambda_c = 260$; 620 nm) and in neutron-irradiated crystals ($\lambda_c = 345$ nm) differ from each other. It was found that in the spectra of PL, GL and TL SiO₂ crystals with Ge and Al impurities, a band of luminescence with a maximum of 680 nm ($\lambda_c = 380$ nm) is observed. It is assumed that it is caused by the recombination of electrons with a hole trapped on the oxygen atom of an impurity germanium tetrahedron. In [13-17], the structure of disordered regions observed in [13] was investigated and it was assumed that their structure is not vitreous. Apparently, there are several varieties of non-bridge oxygen atoms in quartz crystals. At present, the nature of the luminescence centers of the 840 nm band has not been established. It is observed both in pure and impurity neutron-irradiated quartz crystals. This gives reason to believe that it is due to its own structural defect.

5 Conclusions

1. The presence of a glassy phase is not a necessary condition for the stabilization of non-bridge oxygen atoms in crystalline quartz.
2. The observed band with a maximum of 840 nm in the GL, photo- and thermoluminescence spectra of neutron-irradiated crystals is associated with the occurrence of hydrogen ions in the structure of crystalline quartz.

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