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Radiation Effects in Grained Quartz Crystals at Neutron-Irrigited Seeds

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Abstract: *The work is devoted to the growth and study of quartz crystals on irradiated seeds in order to obtain new crystalline substances with given structural and radiation-optical characteristics. The results of studies of X-ray diffraction analysis, photo-gamma-thermoluminescence of crystals after neutron and gamma irradiation are presented. The fraction of the volume of quartz crystals coated with "mixing peaks" at different neutron fluences was calculated, taking into account the attachment of point defects to them. The experimental data on the growth of crystals on irradiated seeds, on establishing the relationship between the structure of the seed and the characteristics of the overgrown layer is of great interest to specialists involved in the creation of materials with desired properties using radiation technologies. A study of the kinetics of the luminescence bands in unirradiated and neutron-irradiated crystals in the temperature range 77–300K revealed luminescence bands 420, 490, 550, 660 nm. The dependence of the intensities of the luminescence bands on the dose of neutron seed irradiation, additional neutron irradiation was determined, and the thermal stability regions of these luminescence centers were determined. It was found that in neutron-irradiated seeds and quartz crystals grown on them, defect centers belonging to the β - phase of quartz exist. The dependences of the concentration of these centers and the β phase on the neutron fluence correlate well with each other.*

Keywords: quartz, seed, crystal, single crystal, radiation, neutron, gamma irradiation, spectrum, luminescence, phase nucleus, band.

Introduction: The foundation of modern science and technology is to obtain materials with predictable properties [1-3]. In this regard, much attention is paid to issues related to the synthesis and growth of crystalline substances. It is known that various structural modifications of quartz (SiO_2) are widely used in various fields of modern science and technology, electronic and radio engineering industries [2-3]. The prospect of their development requires the creation of radiation-resistant and radiation-sensitive crystalline materials, to develop ways to purposefully change their properties using exposure to nuclear radiation. The work presents the results of a study of radiation materials science. [6,9-11].

The purpose and objectives of the research: Study of the effect of radiation-induced structural transformations in quartz crystals grown on neutron-irradiated seeds. To achieve this goal it is necessary to solve the following tasks:

- a comprehensive study of the mechanisms of the formation of point defects, radiation-stimulated phase transformations and amorphization of the structure of quartz crystals under the influence of neutron irradiation;
- the study of changes in the amount of β-phase along the thickness of the growing layer of grown crystals on neutron-irradiated seeds;
- the study of the processes of creating point defects in crystals containing different concentrations of β and amorphous phase nuclei under the influence of neutrons and gamma quanta.

Experimental procedure: Quartz crystals were grown at the Russian Scientific Research Institute of Mineral Raw Materials (RNIISIMS, Aleksandrov) in steel autoclaves (Fig.2) under a pressure of 100 MPa in a 3% NaOH solution using the temperature gradient method (400-350^{0}C. Speed growth of 0.8 mm / day) "at 340 ± 10^{0}C. The seeds were irradiated with neutrons dose 10^{16}-$8*10^{20}$ n/cm^{-2} (VVR-SM nuclear reactor, Institute of Nuclear Physics, Academy of Sciences of the Republic of Uzbekistan (with a neutron flux of $6,5*10^{13}$ n.cm^{-2}sec^{-1} (0.3 hours-4months). Samples - were previously irradiated with γ-rays at a nuclear physical facility of the Institute of Nuclear Physics of the Academy of Sciences of the Republic of Uzbekistan (gamma facility, source Co^{60} (4000 R/s). X-ray diffraction patterns of the samples were taken on a Dron-2 diffractometer using Cu-K_α radiation (λ = 0.1542 nm. The sample was packed in the form of a powder in a standard cell with a layer thickness of 0.5 mm. X-rays scattered by the sample were recorded with a VDS-6 scintillation counter). Photo-gamma-luminescence (PL, GL samples were measured using Specord UV-Vis spectrophotometers (CARL ZEISS, Germany). The GL study was performed on a gamma-ray spectrometer of the INP AN RUz. The GL spectra were recorded on the setup, the main element was SPM-2 spectrograph manufactured by CARL ZEISS, using a photoelectric signal amplifier (PMT-106), in the range of 200-900 nm .This made it possible to register the glow in the region of 300–900 nm. The photoluminescence (PL) spectra and their optical excitation in the region from 200 to 800 nm were measured on a setup assembled on the basis of a xenon lamp with an MDR-12 monochromator (LOMO).

Research results: When studying the crystal structure by X-ray diffraction analysis, assuming that the overgrown layer consists of a mixture of the α- and β- phases, a calibration curve was constructed that allows a quantitative analysis of the composition of the mixture to be performed. For the analysis, the diffraction reflections of $(1120)_{\beta}$ - β phases, which are superimposed on the $(1120)_{\alpha}$ - α phases, and the diffraction reflection $(1121)_{\alpha}$ - belonging only to the α - phase of quartz, were selected. The study of gamma-luminescence (GL) of unirradiated crystals showed that in the temperature range 77 - 200 K there is one band with a maximum of 490 nm (Fig.3). Its intensity decreases at temperatures above 110 K and a band of ~ 420 nm appears at temperatures of 200 K. Irradiation of crystals with neutrons up to 1020 n/cm^2 leads to a decrease in the intensity of the band at 490 nm (Fig.4). At room temperature, the gamma and thermoluminescence spectrum of a quartz crystal grown on a neutron-irradiated dose of $5*10^{18}$ n/cm^2 seed, as in ordinary crystals, is dominated by a band in the region of 520 nm. With an increase in the dose to the seeds, overlapping bands appear with maxima of 460 and 550 nm.

Discussion of results: It has now been established that under the influence of neutrons in the crystalline quartz, the α-β transition [1-3] (Fig.1) and amorphization of the structure [5] are observed. There are basically two assumptions regarding the mechanism of the α-β transition. Many researchers believe [1] that the α - β transition upon irradiation with fast neutron fluences of 4-7 * 10^{19} n/cm^2 occurs without the formation of β - phase nuclei upon reaching a certain concentration of mixed atoms. There is another assumption [6] that the α-β transition occurs through the formation of β-phase nuclei.

The authors of [7] suggest that amorphization of the structure of quartz crystals occurs through the formation of β-phase nuclei. According to the opinion of other authors [8], amorphization is carried out by the accumulation of nuclei in disordered regions.

In our opinion, the study of the structure and radiation - optical properties of quartz crystals grown on neutron-irradiated seeds is the most informative and allows us to elucidate the mechanism of the α-β transition, to study the influence of the structural inhomogeneities of the seed in the form of point defects, β - and amorphous phases on the course of radiation -stimulated processes and physico-chemical properties of the overgrown layer, which is the purpose of this work. To achieve this goal, quartz crystals were grown on neutron-irradiated seeds and their structure was studied. The radiation-optical properties of ordinary crystals (type 1) and crystals grown on neutron-irradiated seeds (type 2) were also studied to study the effect of radiation processing of seeds on the spectral and structural properties of the overgrown layer by gamma-thermo-photoluminescence

In doing so, we proceeded from the following considerations. In [6], it was shown by X-ray diffraction analysis that in crystals irradiated with fluences below $4*10^{19}$ n/cm^2 there is a β phase and its amount increases with the irradiation dose.

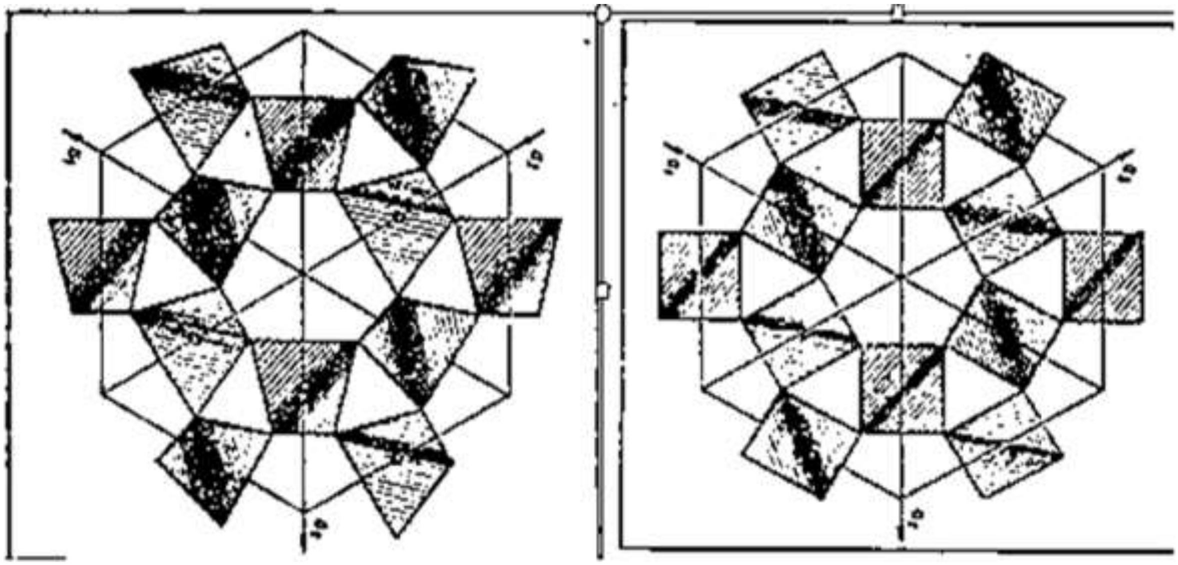

Fig. I. Lattice of the α and β phases of quartz

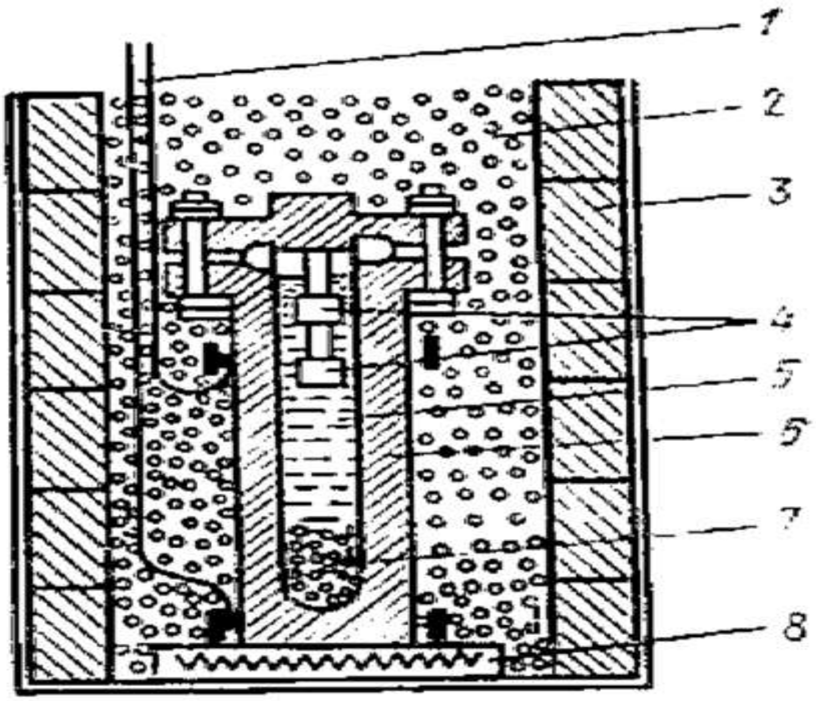

Fig. 2. Scheme of the hydrothermal method of growing (autoclave) quartz crystals

This is in favor of the germinal mechanism of the α - β transition. Therefore, we can assume that if a β-phase is detected in crystals grown on seeds irradiated with neutron fluences below $4*0^{19}$ n/cm^2 and its amount increases with increasing dose of seeds, this is direct experimental confirmation of the nucleating mechanism of the α-β transition. When studying the structure of crystals by X-ray diffraction analysis, assuming that the overgrown layer consists of a mixture of the α and β phases, a calibration curve was constructed that allows a quantitative analysis of the composition of the mixture to be performed. The diffraction reflections of $(1120)_\beta$ - β phases that are superimposed on the $(1120)_\alpha$ - α phases and the diffraction reflection $(1121)_\alpha$ - belonging only to the α - phase of quartz were selected for analysis. The calibration curve for determining the volume fraction of the β - phase is constructed according to the formula

$$K = \frac{J(11\bar{2}0)_{\boldsymbol{\alpha}} * \delta_\alpha + J(11\bar{2}0)_\beta (1 - \delta_{\boldsymbol{\beta}})}{J(11\bar{2}1)_{\boldsymbol{\beta}} * \delta_\beta} \qquad (1),$$

$$\delta_\alpha + \delta_\beta = 1. \qquad (2)$$

where δ_α, δ_β are the volume fractions of α- and β - phases of quartz, $J(11\bar{2}0)_{\boldsymbol{\alpha}}$, $J(11\bar{2}1)_{\boldsymbol{\alpha}}$, и $J(11\bar{2}0)_\beta$ are respectively the integrated intensities of diffraction reflections $(11\bar{2}0)_{\boldsymbol{\alpha}}$, $(11\bar{2}1)_{\boldsymbol{\alpha}}$ и $(11\bar{2}0)_\beta$, we calculate taking into account the structural features of the α and β phases of quartz according to the formula

$$J = K_1 \frac{1 + cos^2 2\theta}{sin^2\theta \, cos\, \theta} |F|^2 P \frac{1}{V^2}, \qquad (3)$$

where θ is the Bragg scattering angle, F is the structural factor, P is the repetition factor, V is the unit cell volume, and K_1 is a coefficient depending on the geometry of the device and determined by the formula

$$K_1 = \frac{e^4 \lambda^3}{32\, \pi\, m^2 \, c^4 R} \qquad (4),$$

here e and m are the charge and mass of the electron, C is the speed of light, R is the distance from the sample to the detector, and λ = 0.1542 nm is the wavelength of Cu-K_α radiation. The calibration curve constructed according to [4] allows one to determine the composition of the α + β phases for any component ratio if the relative intensity of the above reflections is measured. From the calibration curve constructed according to [6], the volume fraction of the β phase was determined that the fluences of the seed irradiation of $5*10^{18}$, 10^{19} and $5*10^{19}$ n / cm^2 are 15, 42, and 46%, respectively. The results showed that in an ordinary neutron-irradiated crystal, i.e. the amount of β phase in the seed is greater than in the overgrown layer.

This is due to competition between the nuclei of the α and β phases during growth and the hindering of the coexisting amorphous phase to the growth of both phases of quartz. These data confirm the nucleation mechanism of the α-β transition and indicate the possibility of obtaining a β phase of quartz that is stable at room temperature. Cracks are observed in crystals whose seeds are irradiated with neutrons with a dose higher than $5*10^{19}$ n/cm^2. The number of cracks increases with the dose of the seed. This is due to the fact that the structure and parameters of the α and β phases of quartz crystals differ from each other (Fig.1).

It is known that the mismatch of the lattice parameters of individual parts of the crystal to each other (heterometry) leads to the formation of cracks. It was previously shown [9] that in ordinary crystals, sectorial distributions of Al and Ge impurities and neutron-induced point defects [10] in quartz crystals grown on neutron-irradiated seeds causes cracks.

The morphology of tracks of high-energy heavy ions in SiO^2 was studied using small-angle X-ray scattering and computer simulation by the molecular dynamics method [14-16]. At a certain threshold value of fluence, the disordering reaches a saturation value of 40 percent, i.e. complete amorphization of the sapphire (Al_2O_3) sample does not occur. In this case, a completely amorphized layer appears on the surface of the sample, the thickness of which grows linearly with an increase in the radiation dose at a rate of the order of 1.3 nm for each 10^{12} cm^2 collected. Comparisons of changes in the intensity of irradiated samples with intensities of an unirradiated sample using the formula

$$F_d = \frac{Xo - X\nu}{1 + X\nu} \qquad (5)$$

the degree of disorder of the irradiated crystal was determined. X_o-normalization of the intensity of the unirradiated sample in the channeling mode, X-intensity of the irradiated sample To determine the model, the dependence of F_d on the fluent is described by the formula

$$Fd = \alpha(1 - e^{-\sigma\phi}) \qquad (6)$$

where the F_d-parameter characterizing the degree of disordering, α- characterizes the degree of maximum disordering, ϕ-fluence, σ-section defect formation, fitting of the values obtained from the formula from formula (5) by formula (6) shows a satisfactory agreement with the experimental data, it is possible to determine the parameters α and σ [17]. In [18], the luminescence and thermal stability of defects formed in α-Al_2O_3 single crystals after intense (300 keV) pulsed irradiation with a C + / H + ion beam were studied. In a wide temperature range of 350–700 K, an intense thermoluminescence band of a complex shape was observed, the intensity of which decreases with increasing ion energy density. The thermal stability of F-type defects formed in α-Al_2O_3 after irradiation with a pulsed ion beam is comparable to that in samples irradiated with neutrons. In [19], yttrium oxide (YSZ) samples grown in three crystallographic orientations 〈100〉, 〈100〉 and 〈111〉. The crystals were irradiated with Ar ions with an energy of 160 keV up to 3 fluences: 1×10^{14}, 1×10^{15} and 1×10^{16}. cm^{-2}. The structural properties of the modified layers were measured using X-ray diffraction (GI XRD) and Raman spectroscopy. The results showed that irradiation with Ar+ions leads to the creation of radiation defects and the localization of voltage caused by damage caused by incoming ions - the magnitude of which may depend on the crystallographic orientation. An X-ray diffraction study in [20] showed a phase change from γ-Al_2O_3: C to α - Al_2O_3: C during annealing of 1573 K. The average particle sizes estimated from XRD peaks and TEM images show an increase in particle sizes from ~ 30 nm to ~ 67 nm. Changes in the luminescence structures of the newly synthesized and annealed phosphorus can be explained by a change in the phase of the crystal structure.

The results of a study of quartz crystals grown on neutron-irradiated seeds showed that in the growing layer there is a β-phase of quartz with lattice parameters different from the parameters of the α-phase. Therefore, plastically deformed regions exist in the overgrown layer at the interfaces of α - and β - phases. These regions are sources of internal stresses and cracks form near the interface between the α and β phases. The coating of quartz crystals grown on neutron-irradiated seeds with an increase in the dose of seeds to the system of cracks is caused by an increase in the number and size of β-phase nuclei. This effect, i.e. inheritance of the β phase by the overgrown layer was called the "Radiation heredity" effect

It was found that at room temperature, the gamma and thermoluminescence spectrum of a quartz crystal grown on a neutron-irradiated dose of $5*10^{18}$ n/cm^2 seed, as in ordinary crystals, is dominated by a band in the region of 520 nm [10]. With an increase in the dose to the seeds, overlapping bands appear with maxima of 460 and 550 nm. This shows that in both types (neutron-irradiated and crystals grown on neutron-irradiated seeds) crystals have the same structural defects.

A study of the GL of unirradiated crystals showed that in the temperature range 77–200K one band is observed with a maximum of 490 nm (Fig.3). Its intensity decreases at temperatures above 110 K and a band of ~ 420 nm appears at temperatures of 200 K. Irradiation of crystals with neutrons up to 10^{20} n / cm^2 leads to a decrease in the intensity of the band at 490 nm (Fig.4).

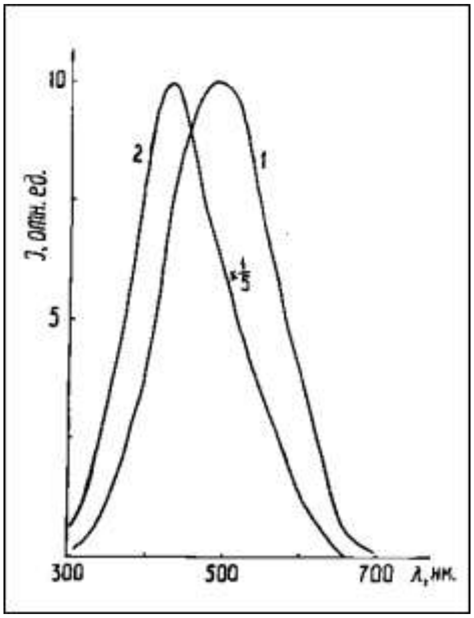

Fig. 3: Low-temperature GL spectra of SiO_2 crystals: Al, 1-77 K; 2 -210 K.

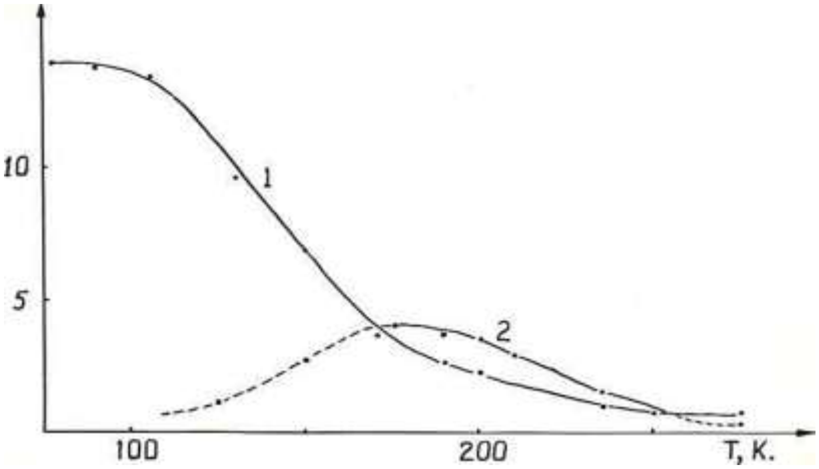

Fig. 4. Dependences of the intensities of the GL bands at 490 nm - 1 and 420 nm - 2 in SiO_2: Al crystals on the excitation temperature.

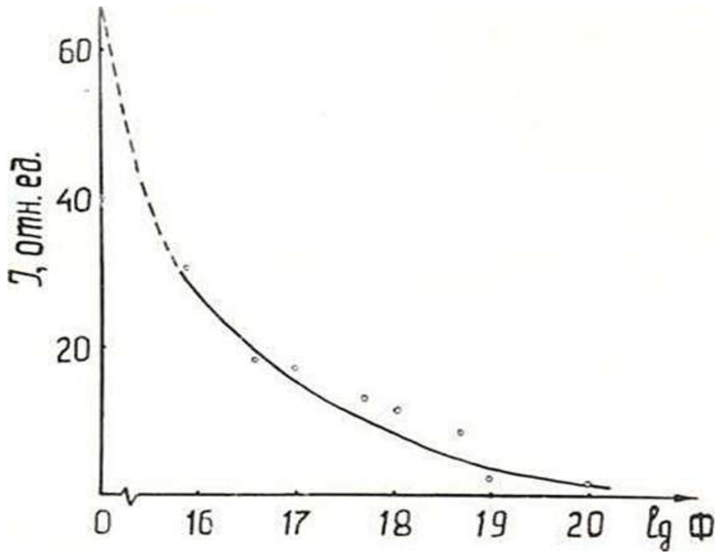

Fig. 5: Dependence of the intensity of the 490 nm band on the dose of neutron irradiation at 77 K.

In the case of crystals grown on neutron-irradiated seeds, its intensity also decreases with increasing fluence of neutron-irradiation of seeds (Fig.5). There are different opinions regarding the nature of the luminescence centers at 490 nm. In [10], it was assumed that it is due to radiative decay of a self-trapped exciton (ALE). At the same time, it was considered in [13] that the luminescence band in the range 470–490 nm is due to electron – hole recombination near impurity aluminum tetrahedra, i.e. in smoky color centers.

The research results showed that the center of luminescence of the 490 nm band is its own structural defect. It arises due to the radiative decay of a self-trapped exciton (ALE) formed by recombination. The decrease in the band intensity with increasing neutron irradiation is due to the obstacle of radiation-induced structural defects to the migration of electronic excitations. In the case of crystals grown on neutron-irradiated seeds, structural defects and β-phases inherited by the bulk layer also prevent migration of electronic excitations, which leads to a decrease in the intensity of the 490 nm band with the irradiation fluence of the seed.The similarity of the dose-dependence of the intensity of the 490 nm band in ordinary and in crystals grown on neutron-irradiated seeds indicates the identity of their structure, i.e. succession to the core layer defects in the structure of the seed.

Defect formation in quartz crystals and crystals grown on neutron-irradiated seeds, having different types of defects and degree of disorder of the structure occurring under the influence of different doses of gamma rays and neutron irradiation, depend on the quality and perfection of crystals . In crystals grown on seeds, irradiated with doses in the range $5*10^{18}$ - 10^{20} n/cm^2, the formation and increase in the number of cracks, violation of homogeneity with increasing radiation dose are observed. The results of calculating the concentration of the β-phase in a neutron-irradiated crystal, studies of the optical properties of neutron-irradiated quartz crystals used as seeds, and the crystals grown on them, along with the proof of the proposed nucleation mechanism of the α-β transition under neutron irradiation showed that the overgrown The layer, together with the β phase, also inherits neutron induced structural defects. The structure of the amorphous phase formed around the β-phase nuclei differs from the structure of quartz glass. The formation of regions with a structure close to the structure of silica glass occurs after certain values of the neutron fluence. Defective centers glowing in the red spectral region were detected in quartz crystals.

Conclusions: Using a set of experimental research methods, it was shown that when growing quartz crystals on neutron-irradiated seeds, the radiation-induced β-phase present on the seed is inherited by the overgrown layer and its concentration increases with increasing seed irradiation fluence (“The effect of radiation heredity”). Direct evidence of the mechanism of the α - β transition in quartz under neutron irradiation is obtained.The results directly confirm the nucleation mechanism of the α-β transition in quartz crystals upon neutron irradiation. Based on the results of a study of the luminescence of ordinary neutron-irradiated without impurity, impurity crystals and quartz crystals grown on seeds irradiated with neutrons, it was established that the presence of an amorphous phase of quartz is not the only condition for the stabilization of non-bridged oxygen atoms, which are the center of the glow in the red region of the spectrum. Non-bridging oxygen atoms stably exist at the interfaces of α - and β - phases of quartz and in the volume of the amorphous phase by its structure close to the structure of quartz glass.

In conclusion, the authors express their sincere gratitude to the RNIISIMS employees for their help in growing quartz crystals on neutron-irradiated seeds, for providing crystalline materials for research and to the staff of the Institute of Nuclear Physics of the Academy of Sciences of the Republic of Uzbekistan for participating in the discussion of the results.

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