SPECTROSCOPIC STUDY OF STRUCTURAL MODIFICATIONS IN CRYSTALLINE SILICA

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Spectroscopical investigations of the radiation-induced structural phase transition in crystalline silica (alpha-quartz) irradiated by various doses of fast neutrons have been carried out. The optical methods of reflectance IR and Raman spectroscopy and the X-ray diffraction method have been used. The regularities for the radiation-induced modifications in the spectral characterictics of some of the bands due to the crystal reconstruction have been revealed, as well as the parameter variations for the bridge bond vibrations of the valence and deformation types. It is suggested that two processes take place during the irradiation: the decay of a part of the Si—O—Si bonds and their deformation, both resulting in a modification of the initial structure. The comparison with the X-ray spectroscopy data on certain parameters and with the Raman spectra obtained at silica heating has been done. The correlation between relevant dependences has been found. The conclusion has been made about the appearance, at the definite stage of the irradiation by fast neutrons, of the state similar to the high-temperature structural modification of quartz.

Quartz of various modifications (crystalline, vitreous) possesses a range of unique properties resulting in its wide-spread usage in optical, electronic, radiotechnical, atomic, and space techniques. In this connection, the experimental and theoretical investigation of the influence of various factors (radiation, temperature, pressure, etc.) on its structure and physical properties is on line [1—9]. We should note that there is little information in the literature about neutron and X-ray investigations of the regularities in co-operative phenomena such as the radiation-induced phase transitions in crystalline silica (quartz). In particular, it is true for neutron-based investigations making use of the vibrational reflectance spectroscopy methods, which defined the aim of the work. The single crystals of the artificial alpha-quartz have been selected as investigation objects. They were exposed to various doses of fast neutron irradiation in the channels of a VVR-SM nuclear reactor at the Institute of Nuclear Physics of the Academy of Sciences of the Uzbekistan Republic. The investigation was carried out with the help of spectroscopic methods: the reflectance IR spectroscopy and the Raman spectroscopy.

Raman spectra are very sensitive to structural modifications of any kind. Therefore, we used just this method to investigate the regularities of the radiation-induced reconstructions in α-quartz. In the literature, we have found a restricted body of information concerning this issue [6—8]. The influence of temperature on the spectra has been studied in [6, 8], and the influence of irradiation — in [8], with the most information concerning a dose of 0.4×10^{19} cm^{-2}. Taking into account the feasible effect of secondary factors on the spectra (the induced coloring in the natural specimen, various geometries of plates, etc.), the experiment was carried out for the series of thin identical plane-parallel plates of the artificial quartz (the Z-cut) of high purity, subjected to the radiation treatment under the monitored conditions.

In Table 1, the dependences of the principal Raman line frequencies in the range 128 to 1162 cm^{-1} on the irradiation dose F are shown. It follows that the radiation influence is extremely low up to $F = 2 \times 10^{19}$ cm^{-2}. The shifts of the spectral maxima occur if F continues to grow. It should be noted that the maximal radiation-induced shift towards the lower frequencies is possessed by a line of 207 cm^{-1}. As concerning the widths of lines, the obtained dependences $\delta(F)$ demonstrate a similar behavior. Moreover, the remarkable spectrum-line broadening in the range 207 to 1162 cm^{-1} occurs during the same irradiation stage. The maximal broadening effect under irradiation has been detected for a line of 207 cm^{-1} as well as for long-wave lines of 466 and 1162 cm^{-1}.

T a b l e 1. Dependence of the Raman frequencies (cm^{-1}) on the irradiation dose by fast neutrons F (cm^{-2})

$F = 0$	$1 \cdot 10^{19}$	$2 \cdot 10^{19}$	$4 \cdot 10^{19}$	$5 \cdot 10^{19}$	$7 \cdot 10^{19}$
207	206	204	194	178	—
265	265	264	264	264	—
357	356	356	355	354	—
396	396	396	398	400	—
466	466	466	462	462	464
697	697	695	698	690	—
796	797	796	796	802	812
1162	1164	1164	1170	1190	—

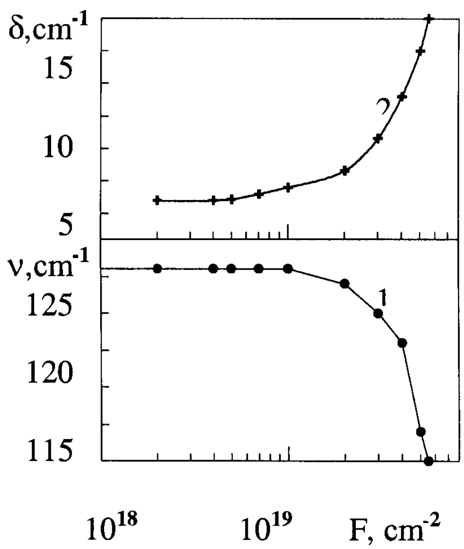

Fig. 1. Dose, F, dependence of frequency (curve *1*) and linewidth (curve *2*) for a line of 128 cm^{-1}

For illustration, the kinetics of spectral characteristics, namely, the frequency ν and the linewidth δ, vs the irradiation dose for one of the "soft" mode (128 cm^{-1}) line is depicted in Fig. 1. It is seen that both functions $\nu(F)$ and $\delta(F)$ vary nonuniformly. Indeed, in the range of doses $F = 1 \times 10^{18} - 2 \times 10^{19}$ cm^{-2}, the line parameters are practically stable, while the parameter values abruptly change for $F > 2 \times 10^{19}$ cm^{-2}, with the change directions being different and the resulting effect being bigger for the second function. It is remarkable that this mode is not observable in the spectrum at $F \approx 7 \times 10^{19}$ cm^{-2}.

Table 2 accumulates the results of estimations carried out for the radiation-induced effects on the intensity, R_I, frequency, R_ν, and the linewidth, R_δ, of the first mode. The obtained values reveal an obvious nonlinearity of the dependences $R_I(F)$, $R_\nu(F)$, and $R_\delta(F)$ for the 128-cm^{-1} mode. On the contrary, those dependences change jumpwise in the range $(2 \div 7) \times 10^{19}$ cm^{-2}, where according to the measured diffractograms, an intense reconstruction of the irradiated crystal occurs. The dependences of those characteristics on the irradiation dose for the second "soft" 207-cm^{-1} mode have a similar nonlinear behavior, which confirms the conclusion about an analogy of the dose dependences of optical and structural parameters of the considered silica.

It is also evidenced by the results of X-ray phase analysis on a diffractometer DRON-3M. The kinetics was traced for the radiation-induced variation of the intensities of the principal reflexes $\bar{3}301$ and $3\bar{3}01$ (see Table 3, Y_1 and Y_2, respectively) which are responsible for the visualization of the α—β phase transition. It was found that at the critical dose $F = 7 \times 10^{19}$ cm^{-2}, the ratio for the intensities of those reflexes $Y_1/Y_2 = 1$ and the crystal lattice parameter $c = 0.545$ nm (see Table 3). These values correspond to the relevant ones for the non-irradiated α-quartz but heated to the temperature of the α—β phase transition ($T_c = 573$ °C). It should be noted that such a correspondence of the α-quartz structural parameters, obtained either due to the irradiation of quartz by the dose F_c or after the thermal treatment of non-irradiated specimens at the T_c temperature, means the completion of the α—β phase transition in a specimen irradiated by the dose F_c.

The results obtained in this work for the peculiarities of the Raman spectra changes for the irradiated specimens and for the parameters of the principal spectral lines were analyzed taking into account the temperature dependences of the Raman spectra for crystalline silica [7]. It turned out that the radiation-induced shifts of the principal line frequencies (128, 207, 265, 357, and 466 cm^{-1}) correlate with the variations of those frequencies with temperature. The dependences of the linewidth on the irradiation dose for lines of 466 and 128 cm^{-1} vary with approximately equal rates. The same behavior was detected also during the temperature elevation up to the temperature T_c of the thermal α—β phase transition in quartz.

Thus, in general, the correlation between temperature- and radiation-induced variations of the

T a b l e 2. Dependence of radiation effects R_i of the 128 cm^{-1} band on fluence F

F, cm^{-2}	R_j, a.u.	R_ν, a.u.	R_δ, a.u.
0	1.0	—	—
$5 \cdot 10^{18}$	1.00	—	—
$1 \cdot 10^{18}$	0.92	0.01	0.4
$2 \cdot 10^{19}$	0.84	0.02	1.0
$4 \cdot 10^{19}$	0.45	0.03	1.8
$6 \cdot 10^{19}$	0.22	0.06	2.6
$7 \cdot 10^{19}$	0.00	—	—

T a b l e 3. Kinetics of the radiation-induced variation of the intensities of the principal reflexes $\bar{3}301(Y_1)$ and $3\bar{3}01(Y_2)$

F, cm^{-2}	Y_1, a.u.	Y_2, a.u.	c, nm
0	4.5	0.2	0.5404
$5 \cdot 10^{18}$	4.4	0.2	0.5404
$2 \cdot 10^{19}$	4.0	0.5	0.5409
$4 \cdot 10^{19}$	3.4	1.6	0.5420
$5 \cdot 10^{19}$	2.9		0.5431
$6 \cdot 10^{19}$	2.7	2.1	0.5444
$7 \cdot 10^{19}$	2.4	2.4	0.5450

spectral characteristics for most lines of the quartz Raman spectrum has been revealed. The spectrum changes drastically up to $F \approx F_c$, where the formation of the stable structure similar to that of the high-temperature quartz modification was registered with the help of X-ray diffractometry.

The influence of irradiation on spectral characteristics of the principal lines of the vibrational spectra of Si–O bonds in the quartz crystal lattice was also investigated by means of reflectance IR spectroscopy. As a result, the essential modification of the reflectance spectrum in the frequency range of symmetric, $\nu_{\rm s}$, and asymmetric, $\nu_{\rm as}$, valence and deformation vibrations of bridge Si—O—Si bonds of the type E has been found, as well as a decrease of their intensities, the change of positions, and the variation of widths of the relevant lines for the dose interval $(2 \div 7) \times 10^{19}$ cm^{-2}, where, according to X-ray phase analysis (see Table 3), an intense phase transition takes place. Therefore, during the neutron irradiation procedure, the destruction and the deformation of principal Si–O bonds take place, accompanied by the breaking of bridge Si—O—Si bonds, the changing of the valence angles Si—O—Si, and the formation of the radicals with dangling bonds. An illustrative example of such a dynamics of the IR spectrum of the radiation-treated quartz is given in Fig. 2. It shows the modification of the spectral characteristics for the first of the listed modes. It is known [9] that in quartz in the high-frequency range of the reflectance spectrum, there is an intense line $\nu_{\rm s}$ possessing the maximum at valence vibrations of Si—O—Si bonds. According to the result obtained (Fig. 2), the increasing of the neutron irradiation dose leads to the decreasing of the peak value of the line reflection coefficient, the line frequency and spectrum profile change, which can be traced up to the dose F_c. In addition, at this critical dose, it was found that the splitting of the second duplet line, $\nu_{\rm as}$, had come to an end and the line with the maximum at 1180 cm^{-1} had disappeared. This result is consistent with the conclusion of Scott et al. [10] about the absence of this mode in the β-phase obtained by heating the non-irradiated crystal up to T_c, and indicates the completion of the radiation-induced formation of the crystalline silica structure, similar to that of the high-temperature quartz modification.

It is seen from Fig. 2 that, during the irradiation of the specimens, the intensity of a line of 797 cm^{-1}, which corresponds to the symmetric valence vibrations of the Si—O—Si bridge bonds, essentially decreases, while the position of the maximum of the reflectance line shifts to lower frequencies; and this process can be traced up to the dose F_c. Basing on the run of the dependences $R(F)$ and $\nu(F)$ for valence and deformation vibrations, one may conclude that the line $\nu_{\rm s}$ is convenient for the quantitative estimation of the reduction of the volume fraction of the α-phase in a heterogeneous phase mixture produced during the irradiation of quartz in a reactor. The absorption frequency of this mode was calculated in the framework of the model of effective oscillator on the plane of complex reflectance amplitudes. According to the results of this calculation, the plot $\nu(F)$ was drawn (see Fig. 3) which demonstrates the extreme shift of the line maximum as a function of the neutron irradiation dose. The conclusion is that the nonlinear relaxation of this parameter, determined for the first time, is stipulated by the α—β phase transition, because the frequency value in the minimum of the dependence concerned (788.5 cm^{-1}) almost coincides with that in the β-phase and the irradiation dose corresponds to the critical one, connected to the structural transformation of crystalline quartz. A similar kinetics is also typical of the dose dependence of the frequency of the deformation mode, extracted from a number of the recorded reflectance spectra of the neutron-treated crystals.

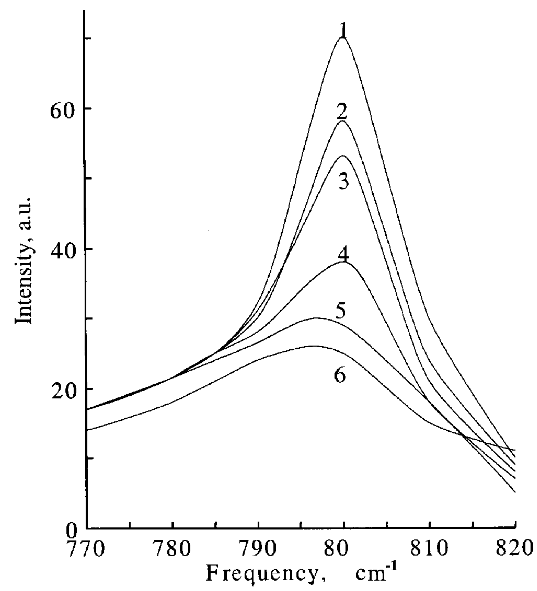

Fig. 2. Influence of the neutron irradiation dose F on the IR spectra of quartz in the frequency range 750–850 cm^{-1}: $F = 0$ (*1*), 2×10^{19} cm^{-2} (*2*), 3×10^{19} (*3*), 4×10^{19} (*4*), 5×10^{19} (*5*), and 7×10^{19} (*6*)

On the basis of the obtained experimental results, a conclusion can be made that during the quartz irradiation in a reactor, two processes take place. The

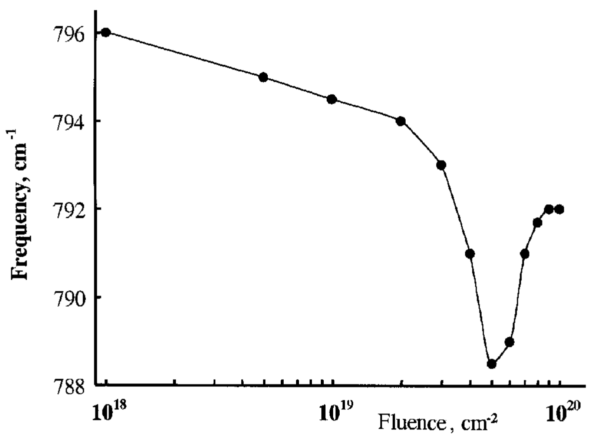

Fig. 3. Dose dependence of the maximum position of the absorption line for symmetric valence vibrations of the crystal

first process is governed by the destruction of a part of the material main frame, which is made up of the tetrahedral molecules of SiO_4, with the destruction resulting from the breaking of Si—O—Si and Si—O bonds. The second one is determined by the deformation of the latter, leading to the stretching of some of the silicon–oxygen bonds (both intra- and intermolecular ones), to the displacement of Si and O atoms, and to the variation of the valence angles of Si—O—Si and O–Si–O. The intensity of those processes increases along with the irradiation dose, and, near the critical value F_c, the parameters reach values which are characteristic of the β-state of the crystal. In accordance with the Saxena's idea that a mode of 207 cm^{-1} is determined by the longitudinal displacements of Si atoms in the base plane and taking into account that its softening by irradiation corresponds to that manifesting at the α—β transition during the heating of quartz, it means that all the results discussed above concerning the neutron irradiation influence on the spectral mode parameters really indicate the major role of Si atom displacements in the phase transition. These displacements transform the defect tetrahedrons into regular ones, the latter being typical of the β-phase structure. Since both modes considered (128 and 207 cm^{-1}) are connected to the intramolecular rotations in Si–O–Si bridges, the revealed drastical changes of their parameters under the irradiation and the disappearance of lines at a certain critical dose F_c verify the completion of the radiation-induced phase transition and the role played in it by the "soft" mode.

It is remarkable that a similar radiation kinetics is observed as well for another degenerate mode of 696 cm^{-1} (E). This mode is a specific line of the valence vibrations of Si—O bonds, is characteristic of the α-quartz structure [9], and disappears near F_c. Probably, such a dynamic of the principal modes is determined by the crystal structure rearrangement, and the relevant dose range should be attributed to the critical one. Indeed, according to the measured X-ray diffraction patterns, as was said above, the rhombohedral structure of the quartz transforms into the hexagonal one at this dose. Moreover, the discovered disappearance of the degenerate modes near F_c, e.g., 1180 and 679 cm^{-1} (E), in the IR spectrum and that of the symmetric mode 207 cm^{-1} (A_1) in the Raman spectrum of the irradiated crystal correlate with the results obtained for the crystal heating up to T_c and with the results of the author's work [10] that the first two modes are inactive in the IR spectrum of the β-phase, while the latter is forbidden by the selection rules in the reflectance spectrum of that phase.

To summarize, we may assert that, due to the action of a certain dose of fast neutrons on the crystalline silica (quartz), a stimulated phase transition into the state similar to the high-temperature one takes place. This transition is accompanied by essential variations of spectral characteristics, in comparison with those of the non-irradiated crystal, which are caused by the breaking and deformation of a part of the silicon-oxygen bonds, and by the changing of the valence angles and lengths of the bridge Si—O—Si and Si—O bonds.

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СПЕКТРОСКОПІЧНЕ ДОСЛІДЖЕННЯ СТРУКТУРНИХ ЗМІН У КРИСТАЛІЧНОМУ КРЕМНЕЗЕМІ

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Р е з ю м е

З використанням оптичних (ІК-спектроскопії відбиття та комбінаційного розсіяння світла) і рентгенографічних методів проведено дослідження радіаційно-стимульованих змін структури, фазового переходу в кристалічному кремнеземі (α-кварці), опроміненому різними дозами швидких нейтронів. Встановлено закономірності радіаційних змін спектральних характеристик деяких полос внаслідок перебудови структури кристала, зміну параметрів валентних і деформаційних коливань міськових зв'язків. Висловлено припущення про те, що внаслідок опромінення кристала відбуваються два процеси: руйнування частини зв'язків Si—O—Si та їхня деформація, — що приводять до зміни вихідної структури. Проведено порівняння даних рентгенівської спектроскопії з окремих параметрів зі спектрами розсіяння, отриманими при нагріванні кварцу; зроблено висновок про кореляцію відповідних залежностей, про формування на певному етапі опромінення швидкими нейтронами стану, подібного високотемпературній модифікації кварцу.