RAMAN STUDIES OF RADIATION-INDUCED MODIFICATIONS IN THE CRYSTALLINE STRUCTURE OF SILICA

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The influence of neutron irradiation on the crystalline structure of silica has been studied by the Raman scattering method. Nonlinear variations of the spectral characteristics have been found for a number of normal vibration modes in the crystalline lattice of silica subjected to high doses of neutron irradiation. The regularities in the radiation kinetics of the corresponding characteristics have been established for certain fully symmetric and degenerate vibration modes. The results obtained are compared with the data concerning the modification of the structural parameters and Raman spectra of thermally treated crystals. A conclusion has been made about the relation between the features revealed in the dose dependences of the parameters of the Raman spectrum modes and the $D_3^4 \rightarrow D_3^6$ reconstruction of the silica crystalline structure.

1. Introduction

New reports devoted to studying the physical properties and the structure of crystalline and vitreous silica, as well as composite materials on their basis subjected to an external influence have been published recently [1–3]. In particular, the influence of neutron irradiation on the vitreous silica structure has been studied in work [1], and the changes in the surface topography of the systems SiO_2 and SiO_2/Si induced by the heat treatment of fused oxide and the layered oxide–semiconductor structure have been considered in work [2]. The authors of work [3] have demonstrated that the strength characteristics of silica glass subjected to electron irradiation are changed, and the degree of corresponding variations depends on the number of point defects in the near-surface layer of glass. At the same time, there are still few works dealing with the comparative study of the influence of high exposure doses of neutron irradiation on the optical properties and the structure of crystalline SiO_2. It is especially true for similar researches, where Raman scattering methods are used. This fact probably takes place owing to the laboriousness of such investigations, which include not only the preparation of a special series of specimens and the fulfillment of spectral measurements, but also the radiation treatment of materials in the channels of a nuclear reactor and the solution of accompanying technical issues.

This work aimed at carrying out the comparative Raman researches of the influence of high exposure doses of fast neutrons on the spectral characteristics of certain fully symmetric and degenerate vibration modes of the silica crystal lattice at a silica polymorphic transformation. The use of Raman techniques allows the microscopic properties of the crystal undergone structural modifications to be studied more accurately.

2. Experimental Part

In this work, we used a structure-sensitive Raman method. The main body of Raman spectra was recorded on a Spex Ramalog installation. An argon laser served as an excitation source. The measurement error was ± 0.5 cm^{-1}.

Artificial silica single-crystals – quartz with a high purity grade (the content of uncontrollable impurities was less than 10^{-4} wt.%) – cut off perpendicularly and in parallel to the optical axis were selected for studies. Measurements were carried out using specially fabricated plane-parallel polished plates $7 \times 7 \times 2$ mm^3 in size. A VVR-SM nuclear reactor served as a source of fast neutrons. The exposure dose was varied in a wide range from 10^{17} to 5×10^{20} cm^{-2}.

3. Experimental Results and Their Discussion

In this work, we continued – by Raman and x-ray spectroscopy methods – the comparative research of the kinetics of radiation-induced damage in crystalline silica specimens subjected to high exposure doses of neutrons. In particular, we studied the features of radiation-stimulated modifications of such spectral characteristics as the intensity J, frequency ν, and bandwidth δ of several fully symmetric and valence vibration modes of Si—O bonds in irradiated plates.

As an example, a series of spectrograms for the same silica single-crystal – non-irradiated and irradiated in the reactor – is depicted in Fig. 1. In the 100–1400-cm^{-1} spectral range of the initial specimen spectrum, there are a number of bands with the maximum frequencies at 128, 207, 265, 357, 396, 466, 697, 796, and 1162 cm^{-1}. In the course of specimen irradiation, the intensities of the peaks vary and their number diminishes, so that the shape of the spectrum changes. The higher is the neutron fluence Φ, the more substantial are those changes (Fig. 1). The growth of Φ is also accompanied by a shift of the majority of the peaks toward lower frequencies. However, the main radiation-induced modifications in the Raman spectrum of quartz occur at $\Phi \approx 7 \times 10^{19}$ cm^{-2}.

In Table 1, the dose dependences of the main Raman line frequencies of the crystal are quoted. The data presented testify that the radiation effect is negligible up to $\Phi = 2 \times 10^{19}$ cm^{-2}; the band maxima become appreciably shifted if Φ grows further. Note that the bands at 128 and 207 cm^{-1} demonstrate maximal radiation-induced displacements, predominantly toward lower frequencies (Table 1). The dependences $\nu(\Phi)$ and $\delta(\Phi)$ obtained for both of those "soft" modes reveal an explicitly nonlinear behavior which is characterized by a drastic acceleration at about $\Phi = 2 \times 10^{19}$ cm^{-2}. Moreover, the amplitude of the radiation-induced effect is greater for the dependence $\delta(\Phi)$. It is remarkable that no vibration mode is observed in the spectrum in the vicinity of $\Phi = 7 \times 10^{19}$ cm^{-2} (Fig. 1 and Table 1): the crystal undergoes a phase transition of the $D_3^4 \rightarrow D_3^6$ type. The results of x-ray phase analysis, which was carried out on a DRON-3M diffractometer, testify to the favor of such an assertion. The consideration of the series of roentgenograms recorded for irradiated quartz crystals allowed us to trace the kinetics of radiation-induced variations of the intensities of main $\bar{3}301$ and $3\bar{3}01$ reflexes (J_1 and J_2, respectively, in Table 2) which are responsible for the visualization of a phase transition of the $\alpha - \beta$ type (it is the phase transition which is characterized by the change of the structure and the symmetry of a crystal according to the $D_3^4 \rightarrow D_3^6$ type). The ratio between the intensities of those reflexes $J_1/J_2 = 1$ and the value of the crystal lattice parameter $c = 0.545$ nm determined at the critical dose $\Phi_c = 7 \times 10^{19}$ cm^{-2} (Table 2) were found to be reproduced for non-irradiated α-quartz heated up to the temperature of $\alpha - \beta$ phase transition $T_c = 573$ °C. It should be noted that such a correspondence between α-quartz structural parameters at either the neutron irradiation of quartz at the dose Φ_c or the heating of non-irradiated quartz to the temperature T_c evidences for a completion of the radiation-stimulated $\alpha - \beta$ phase transition on attaining the exposure dose Φ_c.

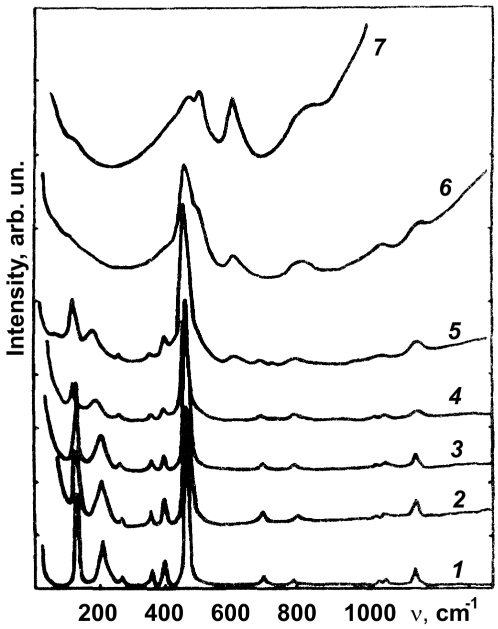

Fig. 1. Raman spectra of α-quartz irradiated with neutrons at various exposure doses: $\Phi = 0$ (*1*), 2×10^{19} (*2*), 3×10^{19} (*3*), 4×10^{19} (*4*), 5×10^{19} (*5*), 7×10^{19} (*6*), and 2×10^{20} cm^{-2} (*7*)

T a b l e 1. Dependences of the Raman band maximum frequency (cm^{-1}) on the neutron exposure dose Φ (cm^{-2})

Frequency	1×10^{19}	2×10^{19}	4×10^{19}	5×10^{19}	7×10^{19}
207	206	204	194	178	–
265	265	264	264	264	–
357	356	356	355	354	–
396	396	396	398	400	–
697	697	698	698	690	–

T a b l e 2. Dependences of the structural parameters on the exposure dose Φ

Φ, cm^{-2}	J_1, rel. units	J_1, rel. units	c, nm
0	4.5	0.2	0.5404
5×10^{18}	4.4	0.2	0.5404
2×10^{19}	4.0	0.5	0.5409
4×10^{19}	3.4	1.6	0.5420
6×10^{19}	2.7	2.1	0.5444
7×10^{19}	2.4	2.4	0.5450

Now, consider the influence of neutron irradiation on the spectral characteristics of other bands in the scattering spectrum of the silica crystals. Let us examine the lines at 466, 357 (both having symmetry type A_1), and 396 cm^{-1} (symmetry type E) in more details. In Fig. 2, the dose dependences of the frequency position

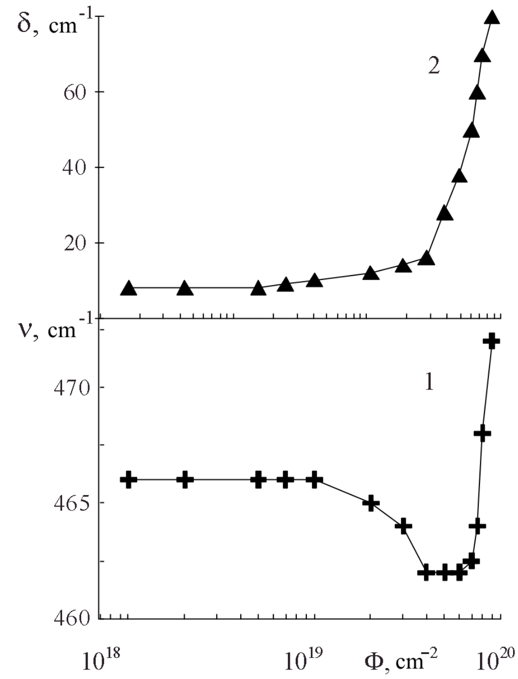

Fig. 2. Dose dependences of the maximum frequency (*1*) and the width (*2*) of the 466-cm^{-1} band

and the width of the 466-cm^{-1} band are exhibited. Curve *2* in this figure demonstrates that the function $\delta(\Phi)$ changes weakly up to the dose $\Phi = 10^{19}$ cm^{-2}. But, at $\Phi > 2 \times 10^{19}$ cm^{-2}, this function reveals a step-like increase, i.e. the slope of the curve changes drastically at about $\Phi = 4 \times 10^{19}$ cm^{-2}. Such a behavior at the first stage of irradiation is also observed for the other parameter of the mode, its frequency. But, at the second stage of irradiation, the character of the $\nu(\Phi)$-curve profile changes (curve *1*): this parameter relaxes. Moreover, this dependence reveals a "plateau"-like feature in the interval $\Phi = (4 \div 6) \times 10^{19}$ cm^{-2}; afterwards, the process of mode softening sharply stops, and the band maximum frequency becomes growing (Fig. 2, curve *1*) up to the dose $\Phi = 2 \times 10^{20}$ cm^{-2}. Such a behavior testifies that the radiation kinetics of one of the parameters of crystal lattice deformation vibrations of the A_1 symmetry type is not monotonous but passes through an extremum; this occurs when a "plateau" section appears in the corresponding plot.

It should be noted that the feature of the radiation-induced effect for the frequency position of the fully symmetric 466-cm^{-1} mode, which was established for the first time in this work, and the feature (in a "plateau"-like form) found by us earlier in the spectrum of the red photoluminescence of neutron-irradiated crystals (the photoluminescence is due to the generation of point defects of the non-bridge oxygen atom type ($Si–O_1^0$ in the material), when neutrons displace oxygen atoms by the impact mechanism and break Si—O—Si bridge bonds) are observed at the same stage of material irradiation. Relying on this fact, we may draw a conclusion that the examined features in the variation of Raman spectral characteristics of the fully symmetric vibration in silica, which are observed at a definite stage of neutron irradiation of the crystal, may be probably related to the accumulation of radiation-induced defects up to a certain concentration, the modification of the crystal structure state, and, as a result, a change of the light scattering by crystals.

To verify this conclusion, we compared our experimental data with the temperature dependences of the parameters under consideration for the 466-cm^{-1} band [4, 5] presented in Table 3. While analyzing the dose (Fig. 2) and temperature (Table 3) dependences of the frequency and the width of the 466-cm^{-1} band, we may point out that both kinetics (radiation- and temperature-induced ones, i.e. taking either surface or bulk effects into account) are correlated to some extent. The correlation includes both the intense softening and broadening of this deformation-induced scattering band in the vicinity of either the temperature T_c or the exposure dose Φ_c, which corresponds to the $\alpha - \beta$ phase transition (stimulated by either heat treatment or irradiation, respectively) in the crystalline silica. Moreover, the relevant δ-values of the given mode at T_c and Φ_c are equal.

We also found the features of radiation-induced effect in the dependences $\Delta\nu(\Phi)$ and $\Delta\delta(\Phi)$ for the second fully symmetric vibration mode at 357 cm^{-1} (symmetric type A_1) in neutron-irradiated crystals. From the comparison of those dependences, it follows that the shift directions of these quantities are opposite to each other, and the rate of radiation-induced band broadening increases at

T a b l e 3. Temperature dependences of the maximum frequency ν and the width δ of the 466-cm^{-1} band. Subscript 1 corresponds to the data of work [4], and subscript 2 to the data of work [5]

T, °C	ν_1, cm^{-1}	δ_1, cm^{-1}	ν_2 cm^{-1}	δ_2, cm^{-1}
25	466	12	466	13
200	464	20	462	15
350	457	30	459	22
500	454	40		
600	453	48	458	35
700			460	36
800			462	37

$\Phi > 2 \times 10^{19}$ cm^{-2}, as it was for the first line. But the maximum frequency of the second band becomes drastically lower at this irradiation stage. Therefore, a conclusion can be drawn that the radiation kinetics of the spectral characteristics of the vibration modes at $466(A_1)$ and $357(A_1)$ cm^{-1} in crystalline silica correlate with each other, although the amplitude of the radiation-induced effect is more pronounced for the first mode.

There is one more feature in the dynamics of the crystal lattice of the irradiated material in the indicated range of its Raman spectrum. Namely, if the specimen is irradiated to the critical dose $\Phi_c = 7 \times 10^{19}$ cm^{-2}, the second band is absent from the spectrum. The selection rules allow both vibrations of the A_1 type (at 466 and 357 cm^{-1}) to manifest themselves in the Raman spectrum of the silica trigonal α-phase. At the same time, in accordance with calculations, the selection rules forbid the manifestation of the second vibration mode (the $357(A_1)$-cm^{-1} band) in the spectrum of the β-phase. Therefore, the disappearance of this band in the vicinity of Φ_c, which was registered in our experiments, testifies to the completion of a phase transition of the $\alpha - \beta$ type at the given irradiation stage.

We also studied the crystal lattice dynamics of neutron-irradiated specimens in the range of one of the degenerate vibration modes, in particular, at 396 cm^{-1} (symmetric type E). It turned out that the features of the dose dependences $\Delta\nu(\Phi)$ and $\Delta\delta(\Phi)$, which were described above for the band $357(A_1)$ cm^{-1}, remained the same for the band $396(E)$ cm^{-1}. In addition, for the exposure doses of about Φ_c, this band disappears from the Raman spectrum. This fact correlates with the absence of this band in the spectra of specimens heated up to T_c and with the zero dipole moment of the degenerate mode in the β-phase. Thus, we possess one more confirmation that the process of radiation-induced phase transition becomes completed at this stage of the material irradiation.

We made an approximation of the dose dependence of the $396(E)-$cm^{-1} band intensity. The corresponding analytical expression looks like

$$J \approx \text{const}|\Phi_c - \Phi|^{-k}, \tag{1}$$

where Φ and Φ_c are the exposure dose and the critical exposure dose, respectively; k is the exponent of the sought function; and J is the band intensity. Formula (1) can be used while describing the radiation kinetics of the relative variation of the degenerate mode $396(E)$ cm^{-1} intensity; in this case, the value of the exponent in Eq. (1) is close to unity. From the results of work [7], it follows that, while considering thermal phase transitions, the expression describing the variation of the light scattering intensity of this mode in the vicinity of T_c is close to expression (1). This result obtained for the degenerate mode intensity is of interest, because it is an extra confirmation of the fact that the modification of the phase state of crystalline silica becomes completed if the exposure dose Φ_c has been achieved.

This conclusion is based on the following assumption. One may talk about the phenomenological comparison between the radiation- and thermal-induced phase transitions as far as it is valid for the increase of the exposure dose at irradiating a material and the temperature rise at heating it. The confronting of the critical values for the irradiation dose Φ_c and the heating temperature T_c is formal, because the analogy is observed only with respect to the final results of a transition, whereas the physics of those processes are different.

Note that the IR spectra measured for a series of neutron-irradiated specimens reveal – in the range of the $396(E)$-cm^{-1} valence mode – the same features in the dose dependences of their spectral characteristics, as the Raman spectra do. The disappearance of the band is observed at the specimen irradiation to the dose Φ_c, as in the Raman spectrum case (Table 1). This fact is another confirmation that the radiation-stimulated phase transition in irradiated quartz becomes completed at the indicated exposure dose.

It is known that the vibration spectrum bands in the range $350 \div 500$ cm^{-1} are related to deformation vibrations (for instance, the $466(A_1)$-cm^{-1} band), rotations, bends directed normally to the O—Si—O plane, atom displacements, and changes of the valence angles of the Si—O—Si and O–Si–O bonds in tetrahedra [8] (the $396(E)$- and $357(A_1)$-cm^{-1} bands). This fact, taking into account the regularities of radiation-induced modifications to the spectral characteristics of the considered fully symmetric and degenerate vibration modes in crystalline quartz irradiated with neutrons, which were established in this work, testifies that the neutron irradiation gives rise not only to the destruction of the Si—O—Si- and Si—O bonds, but also to their substantial modification caused by the deformation of Si—O—Si bridge bonds and valence angles owing to the bend and rotation of the basic bonds, Si and O atom displacements, accumulation of radiation-induced defects and damages in the material, destruction of some part of the main skeleton and intramolecular Si–O bonds that stimulate – in quartz – a phase transition of the $\alpha - \beta$ type, when the crystal symmetry becomes higher ($D_3^4 \rightarrow D_3^6$).

The approximation of the known dependence $\delta(T)$ [4] for the scattering band $466(A_1)$ cm^{-1} brought about the following expression:

$$\delta(T) = \delta_1(T_1) + \delta_2(T_2), \tag{2}$$

where δ_1 and δ_2 are the band broadenings at temperatures $T_1 < 543$ K and $T_2 > 543$ K, respectively. We arrived at a conclusion that the second term on the right-hand side of formula (2) is dominant near the phase transition temperature. This result agrees with the result of work [8], where two reasons for the thermal broadening of Raman bands were supposed, anharmonicity and molecular reorientation. The corresponding height of the potential barrier U for the tetrahedral molecule reorientation at the phase transition was calculated to be 0.04 eV.

While analyzing the obtained dose dependences of the $466(A_1)$-cm^{-1} band, the following relation was found for the second addend in formula (2) describing the variation of the deformation vibration bandwidth:

$$\delta(\Phi) = A\exp(-B\Phi). \tag{3}$$

Here, A and B are the factors to be found empirically. This term becomes dominant near the critical irradiation dose at the stage of an intense radiation-stimulated transition of the $\alpha - \beta$ type. All that evidences for the prevailing role – as compared with that of the anharmonicity of vibrations – of molecular reorientation, together with displacements of atoms at crystal lattice sites, in the broadening of the $466(A_1)$-cm^{-1} band in the Raman spectrum at the radiation-induced $\alpha - \beta$ phase transition in crystalline quartz. The contribution of atomic displacements may be quite appreciable, if one takes into account the amplitude of the potential barrier obtained above, which turned out close to the value of 0.05 eV quoted in work [9] for a barrier which is overcome by charge-compensating ions at the radiation-stimulated diffusion in tetrahedral molecules of the irradiated crystal.

4. Conclusions

The effect of the neutron irradiation on the Raman spectra of silica has been studied. The regularities in radiation-induced modifications of the intensity, frequency, and bandwidth of certain fully symmetric and degenerate vibration modes of the crystal lattice have been established. An analogy between the lattice dynamics data for the irradiating and the heating of specimens has been found. A conclusion has been drawn that the discovered nonlinear effects of radiation-induced modifications of the spectral characteristics of certain bands in the silica Raman spectrum, as well as the disappearance of some of them, are caused by changes of the crystal structure. The power dependence has been found for the radiation-induced variation of the degenerate vibration mode intensity, and the exponential one for the broadening of the fully symmetric mode. A supposition has been made that the radiation-stimulated phase transition in studied silica originates from the displacements of atoms located at the crystal lattice sites, lattice deformation, and molecular reorientation.

1. J.B. Bates, E.W. Hedricks, and L.B. Shaffer, J. Chem. Phys. **61**, 4163 (1974).
2. N. Tokuda, M. Murata, and D. Hoja, Jpn. J. Appl. Phys. **40**, 4763 (2001).
3. D.Yu. Biryukov, A.F. Zatsepin, and V.S. Kortov, Fiz. Khim. Stekla **27**, 495 (2001).
4. P.R. Narayanaswamy, Proc. Ind. Acad. Sci. A **28**, 417 (1948).
5. L.P. Osipova, T.V. Smirnova, and S.V. Ivanova, Izv. Vyssh. Ucheb. Zaved. Fiz. **32**, 105 (1989).
6. J.P. Scott and P. Porto, Phys. Rev. **161**, 903 (1967).
7. V.L. Gertsberg, A.P. Levanyuk, A.A. Sobyanin, Usp. Fiz. Nauk. **130**, 615 (1980).
8. M.M. Sushchinskii, *Raman Spectra of Molecules and Crystals* (Israel Program for Scientific Translations, New York, 1972).
9. V.E. Khadzhi, L.I. Tsinober, L.M. Shetennlikht et al., *Synthesis of Minerals* (Nedra, Moscow, 1987) (in Russian).

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ДОСЛIДЖЕННЯ МЕТОДОМ КОМБIНАЦIЙНОГО РОЗСIЯННЯ СВIТЛА РАДIАЦIЙНИХ ЗМIН КРИСТАЛIЧНОЇ СТРУКТУРИ КРЕМНЕЗЕМУ

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Р е з ю м е

Методом комбiнацiйного розсiяння свiтла (КРС) дослiджено вплив нейтронного опромiнення на стан кристалiчної структури кремнезему. Виявлено нелiнiйнi ефекти змiни спектральних характеристик ряду нормальних коливань кристалiчної ґратки пiд дiєю великих доз нейтронного опромiнення. Визначено закономiрностi радiацiйних кiнетик вiдповiдних характеристик для деяких повносиметричних та вироджених мод. Отриманi результати порiвняно з даними вимiрювання параметрiв структури i спектрiв КРС термооброблених кристалiв; зроблено висновок про зв'язок виявлених особливостей дозових залежностей параметрiв дослiджених мод у спектрi КРС з перебудовою структури кристала по типу $D_3^4 \to D_3^6$.