

## **Effect of Irradiation on Optical Properties of Materials for Synthesis of Thermoregulating Coatings**

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**Abstract.** The paper presents some results of the research on the effect of UV irradiation on optical properties of materials (sodium and potassium silicates) for thermoregulating coatings (TRC) obtained from various rocks (diatomite, perlite) by hydrothermal-microwave synthesis. It is shown that UV radiation contributes to redistribution of the absorption intensity peaks responsible for defect formation in the crystal lattice. Absorption measurements of obtained materials for TRC irradiated at low temperature (-100°C) have shown that the intensity of silicate bond oscillations decreases because of the amplitude decrease due to "freezing" (in this case, the structure of spectra is preserved). When irradiated at high temperature (150°C) the picture is changed due to the fact that under UV irradiation, a "radiation annealing" takes place that contributes to stability of certain structural disorders.

**Keywords:** UV radiation, sodium and potassium silicates, thermoregulating coating, perlite, diatomite, optical absorption, defects

### **1. Introduction**

One of the most important tasks in the field of space materials science is the study of changes in the structure, optical and other properties of pigments in the thermoregulating coatings (TRC) of space vehicles (SV) under the influence of various types of radiation (solar ultraviolet, protons, electrons, etc.). Various lattice defects that occur during irradiation are responsible for the changes. They decrease the reflectivity of the pigments and lead to increase in the integral absorption coefficient. Identification of types of the induced radiation defects and study of the mechanisms of their formation are most important problems when controlling properties of thermoregulating coatings [1- 8].

Therefore, an effective method of combating radiation-induced effects (breakdowns) is a proper choice of materials for SV external surfaces with high resistive and dielectric properties, dielectric strength, reduced tendency to accumulate charges and the ability to their rapid relaxation. At the same time, physical properties must be maintained at an acceptable level for a long period of radiation and thermal influences of the space environment. Solution of this problem also requires corresponding accelerated simulation tests [9-10].

When studying the joint and separate effects of UV-radiation, electrons and protons, the authors [3-5] have revealed non-additivity of the joint action. To identify its reasons, a detailed study of the mechanisms of radiation defect formation in the TRC pigments exposed to various types of ionizing radiation as well as their combined effect is needed. Therefore it is advisable to use the methods of physical modeling for a comprehensive research of the behavior of space vehicle coating materials under the conditions of ground forced exposure to major space environment factors (SEF): high vacuum, streams of high energy charged particles, electromagnetic solar radiation, thermal cycling, etc. [7,8]. The active thermoregulating system presents a special shutter

assembly connected by a piping system filled with a working medium, liquefied gas. Depending on the thermal load, the opening angle of the shutters and, accordingly, the amount of the heat removed into space is changed. Such systems are bulky, weighty and require special control. Therefore, along with them, it is necessary to use some passive thermoregulating systems that don't require permanent control [7-9].

There are number of compositions for "solar reflectors" type thermoregulating coatings including enamel and ceramic coatings on the basis of pigments with organic and inorganic binders applied to the external surface of space vehicles. The temperature of space vehicles with the passive thermoregulation is determined by the amount of absorbed solar energy, which depends on the integrated absorption coefficient of solar radiation and the amount of heat generated by onboard equipment and radiated into space. In SV, the largest areas are just the stable thermoregulating coatings of "solar reflectors" type, which are intended to reflect electromagnetic solar radiation and re-emit the heat generated by onboard equipment into the space [10,11].

The radiation resistance (resistance to UV, gamma ray irradiation, electron- and proton beam, etc.) and optical properties of the TRC materials are influenced by the surface, structure and pigment powder particle size, quality and quantity of the elements used to modify their properties. When working under extreme space conditions, TRC physical, mechanical, and chemical characteristics are changed, thus reducing their lifespan.

The problem of increasing the radiation resistance of pigments for TRC in extreme conditions can be addressed in different ways: the development of new compositions, modifications, production of pigments with appropriate structure and particle size.

From the analysis of scientific and technical literature it is known that the materials for space vehicles are mainly produced on the basis of the white oxide pigments [11-15]. These materials are obtained based on expensive high-purity chemicals by modification of nanopowders of certain compositions at high temperatures. The multi-stage process of their obtainment is time-consuming and inefficient. Therefore, there is a need to develop new compositions and fundamentally new methods for their production using cheap materials for the manufacture of TRC.

The aim of this work is to study the influence of ultraviolet (UV) radiation on optical properties (absorption) of sodium and potassium silicates for thermoregulating coatings obtained by hydrothermal-microwave (HTMW) method from rocks-diatomite, perlite, quartzite.

## **2. Materials and methods**

From the literature it is known that the glass industry is very interested in high-silicon amorphous rocks (opal cristobalite rocks) as an alternative source of silica-containing raw materials, in particular, quartz sand. These rocks include diatomites, gaizes, tripolites, obsidians, perlites, pitchstones, spongiolites, radiolarites [7-10]. The main advantage of opal cristobalite rocks is a high content of amorphous silicon dioxide phase (up to 70% of amorphous SiO<sub>2</sub>). Biogenic structure of the silica of opal cristobalite rocks causes anomalous properties as compared to the artificial amorphous silica and finely crystalline quartz. Of all the representatives of the opal cristobalite group, diatomites are the most promising raw material for obtaining thermoregulating coatings as they have more stable chemical and mineralogical composition due to the specific conditions of formation.

Perlite is a loose earth or semiconsolidated, porous and light sedimentary rock, formed mainly by siliceous fragments of armors (skeletons) of diatomic algae: diatoms and radiolarians. The

main part of the silica armor (skeleton) is silica hydrates of varying degrees:  $m\text{SiO}_2 \cdot n\text{H}_2\text{O}$  type opals.

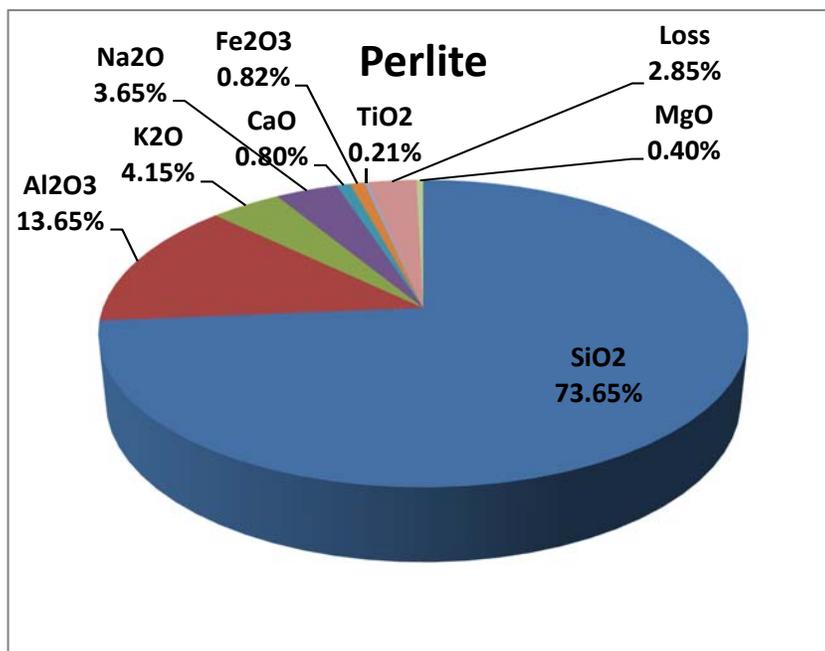


Fig. 1. Chemical composition of initial natural samples of perlite measured by XRF.

It is known that natural rocks have a certain petrochemical composition formed in certain geological conditions and are characterized by varying radioactivity. The basic prerequisite of the rocks radioactivity is the availability of uranium, thorium, and their decay products, potassium and rubidium in the rocks.

The presence of radioactive elements such as thorium and uranium and their families in perlites led to the necessity to study the radioactive properties of the rock with a view to develop some recommendations for their use as raw materials when producing silicate solutions for TRC.

The subjects of research were perlites of various density: porous ( $1400 \text{ kg/m}^3$ ), semidense ( $1600 \text{ kg/m}^3$ ), and dense ( $1900 \text{ kg/m}^3$ ) varieties.

Table 1. presents comparative data on percent abundance of radioactive elements in acidic crustal rocks and their content in perlites of Aragats deposit[16,17].

Table 1. The amount of radionuclides in perlites

Rock characteristics	U, wt.%	Th, wt.%	K, wt.%	Rb, wt.%
Abundance of acid rocks	$3.5 \cdot 10^{-4}$	$18.0 \cdot 10^{-4}$	3.34	-
Perlite: $1400 \text{ kg/m}^3$	$2.9 \cdot 10^{-4}$	$22.0 \cdot 10^{-5}$	3.8	$3 \cdot 10^{-3}$
$1600 \text{ kg/m}^3$	$3.8 \cdot 10^{-5}$	$25.0 \cdot 10^{-5}$	3.0	$3.0 \cdot 10^{-3}$
$1900 \text{ kg/m}^3$	$2.4 \cdot 10^{-4}$	$22.0 \cdot 10^{-5}$	4.0	$5.0 \cdot 10^{-3}$

The sample radiometry was carried out using both UMF-3 type low background-type device (“cuvettes” method) and UMP-1500M in the case of thick sample layer. The detector counters SI-16 and SBT-13 respectively were used.

Table 2 shows the specific and effective specific activity of perlites, as well as the content of radionuclides in perlites of Aragats deposit.

Table 2  
Specific and effective specific activity in perlites of Aragats deposit.

Perlite rock characteristics	Specific activity, Cu/g			
	<sup>228</sup> Th	<sup>226</sup> Ra	<sup>40</sup> K	C <sub>ef</sub>
1400 kg/m <sup>3</sup>	<sup>228</sup> Th	<sup>226</sup> Ra	<sup>40</sup> K	C <sub>ef</sub>
1600 kg/m <sup>3</sup>	1,9	3,0	26	7,7
1900 kg/m <sup>3</sup>	1,6	2,2	30,0	6,8
Heat-treated perlite	2,5	2,8	31,0	8,7

Table 3  
The content of natural radionuclides in perlite samples

Sample	Specific activity, Bq/kg							
size, mm	-40	<sup>238</sup> U series			<sup>232</sup> Th series			<sup>32</sup> Th
		i-214	b-214	a-226	b-212	c-228	<sup>08</sup> Tl	
Average density of 1009 kg/m <sup>3</sup>								
2,5-5,00	20	7,3	8	8	8	2	9,4	48,7
1,2-2,50	27	2	8	02	3,5	0	2,0	44,5
0,63-1,25	32	9	4,5	26	8	4	1,3	48,6
0,31-0,63	39	7	0	44	5,7	9	5,7	34,3
0,14-0,31	018	0	4	2	6	1	0,4	47,8
Average	67	3.3	9.1	05	4.4	1.2	5.7	44,78
Average density of 1300 kg/m <sup>3</sup>								
2,5-5,00	207	1,4	7,3	20	5,5	4,6	06,2	40,2
0,6-1,25	246	6,5	0,8	28	2,4	4,7	2,6	30,5
0,14- 30	228	2,2	9,5	24	1,4	4,4	9,8	44,9
Average	227	3.7	9.2	24	3.1	4.56	6.2	38.53

Average density of 1616 kg/m <sup>3</sup>								
2.5-5.0	046	9,0	4,2	20	9,9	0,4	13	42,0
1.2 - 2.5	75	4,7	3,2	5,4	0,2	0,4	03	39,4
0.3-0.6	028	5,4	5,2	12	9,0	0	23	45,6
0.6-1.2	2,8	5,6	05,6	3,7	3,1	00	2,3	62,8
0,14-0,31	0,6	3,3	92	5,7	7,1	30	0,9	70,6
Average	065	2.5	6.3	21	1.7	4.2	13.8	2.04
Average density of 1964 kg/m <sup>3</sup>								
2.5-5.0	32	8	6,2	23,8	3,7	9	7,0	45,2
1.2 - 2.5	14	4,5	8,3	36,8	7,0	1,6	4,3	39,1
0.6 - 1.2	95	7,4	5,8	8,5	7,4	3,6	1,5	40,6
0.3-0.6	97	4,6	7,5	9,2	9,9	6,8	9,8	42,7
0,14-0,3	62	0,5	6,2	1,4	9,5	6,0	2,7	43,5
Average	40	1	6.8	10	9.5	5.4	7.06	2.22

It is possible to conclude from these figures that the perlite with such radioactive properties is a successful raw material to produce silicates.

We studied the effect of UV irradiation on the radiation-optical properties the precursors (*obtained from perlite* by hydrothermal-microwave synthesis) of thermoregulating coatings within the wavelength range from 1 to 2.2  $\mu\text{m}$ . UV radiation within the spectral region of 240-320nm was carried out using 1 kW DKsEl-1000-5 xenon lamp. Before the irradiation, the samples of sodium and potassium silicates, obtained by hydrothermal microwave (HTMW) processing of rocks, were dried in drying cabins until powdering. UV irradiation was carried out using various exposures and cycles and lasted up to 180 minutes. After UV irradiation, the samples mixed with KBr (mass fraction of the tested substance in the tablet was about 25%) were pressed into tablets. In more detail: the sample, a powdered test substance mixed with KBr in the ratio of 130:30 mg, was milled and pressed into a tablet 20 mm in diameter using a specially designed compression mould. To eliminate the effect of KBr that often distorts the appearance of the absorption bands, the measurements were carried out in a two-beam mode: a control KBr tablet made in the same conditions as the test sample was placed in the comparison channel. The transmittance/absorbance spectra were measured at various time intervals after irradiation.

### 3. Results

The results of the carried out research show that the behavior of the transmission (absorption) spectra of sodium and potassium silicates samples depends on the composition of the silicate (Fig. 2, 3). The absorption at 1.3 microns with a pronounced maximum for sodium silicate and a weak one for potassium silicate is explained by the presence of valence vibrations of water  $\mu(\text{OH})$  or perhaps by their own structure in the non-irradiated samples.

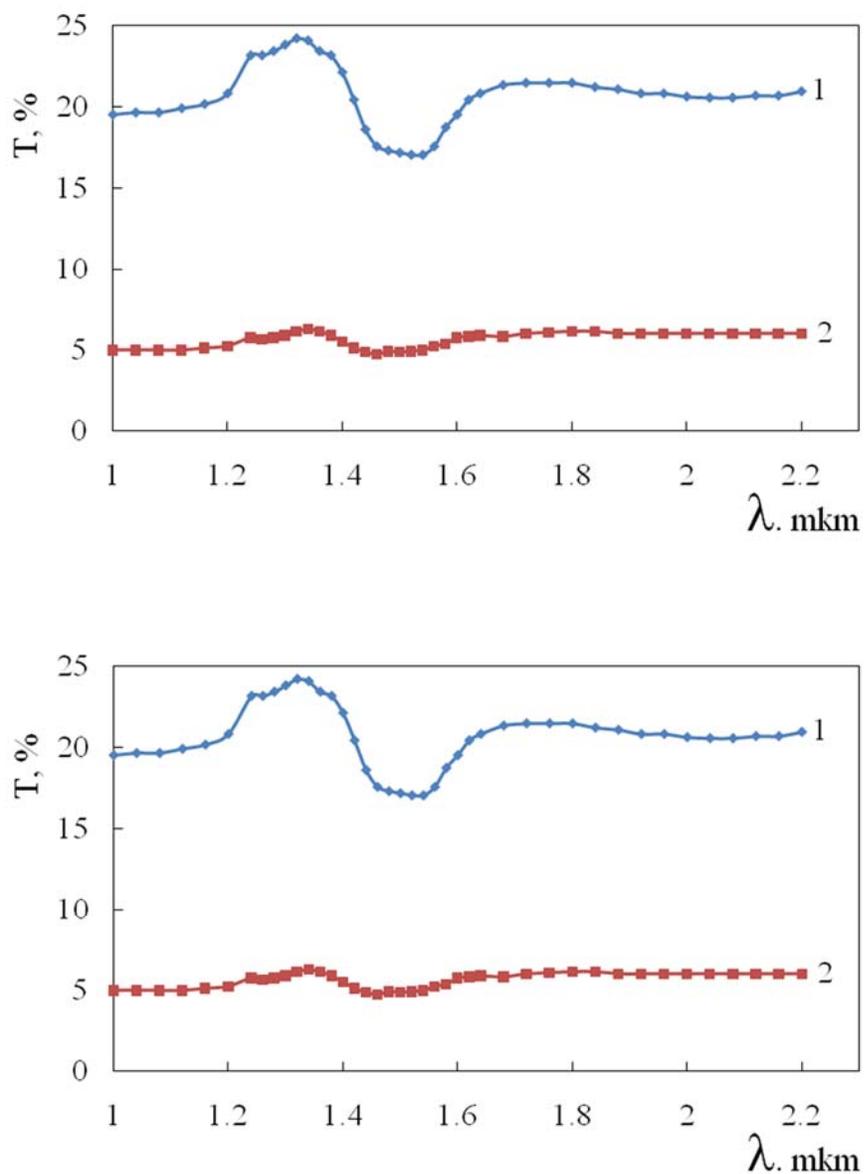


Fig. 2. The optical transmission (absorption) spectra of the initial samples obtained by HTMW processing of diatomite: 1- sodium metasilicate; 2- potassium tetrasilicate.

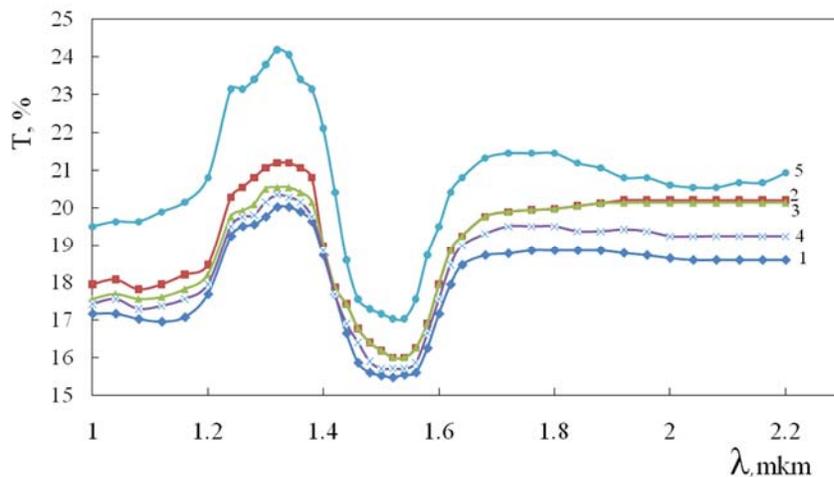


Fig. 3. The optical transmission (absorption) spectra of sodium metasilicate obtained from diatomite, after UV irradiation: 1- irradiated for 30 minutes; 2 - irradiation for 30 minutes, measured 150 hours after irradiation; 3 –irradiated and measured repeatedly 7 days later for 60 minutes (total irradiation time made 90 minutes); 4 - irradiated for another 60 minutes and measured (total irradiation time made 150 minutes); 5 - original sample.

The possible presence of water in the structure is indicated by the deformation vibrations (OH) at 1.4 μm 1.6 μm. After UV radiation within the wavelength region of 240 – 320 nm, some decrease in intensity of the transmission peaks was revealed in the samples.

Figures 4 (a, b) show the transmission (absorption) spectra of the samples of sodium and potassium silicates.

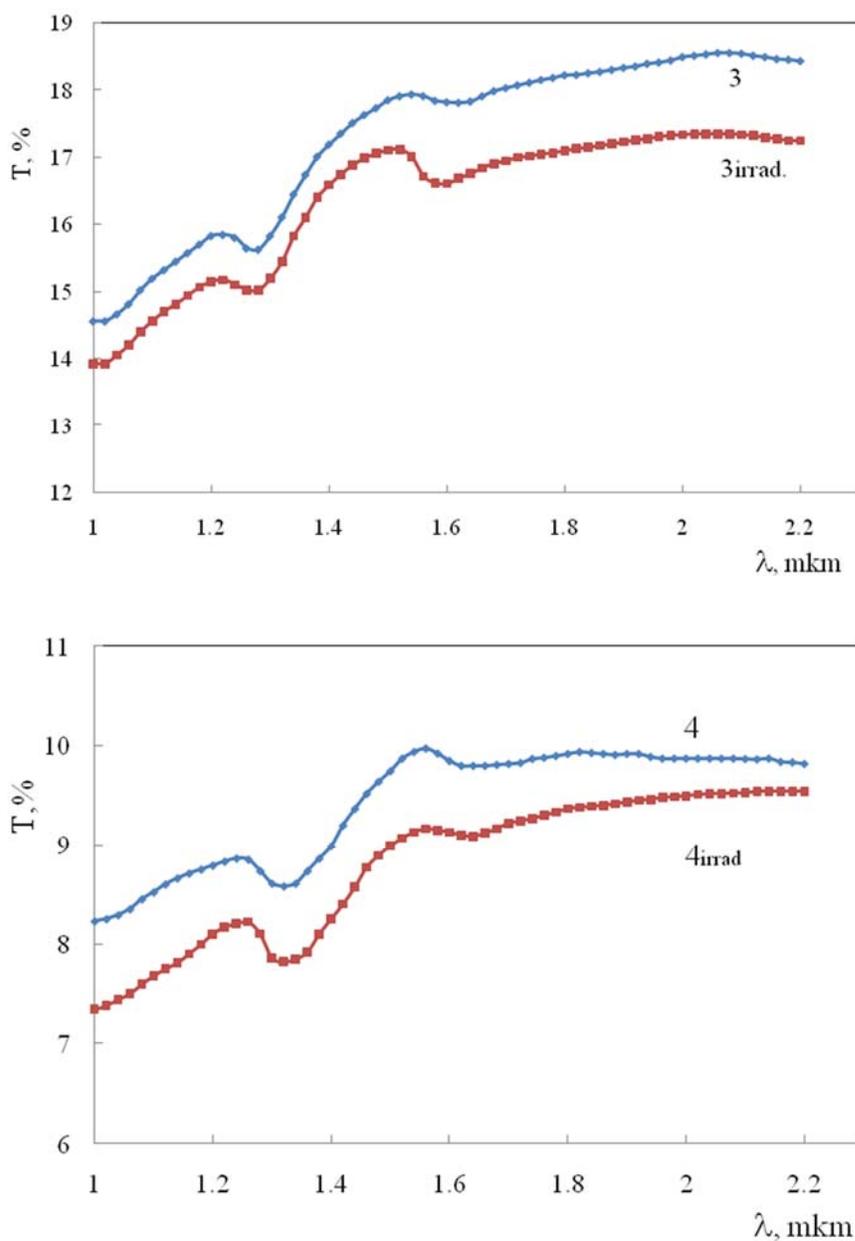


Fig. 4(a, b). The transmission spectra of the initial non-irradiated samples obtained by HTMW treatment of perlite (curve 3: sodium silicate powder, curve 4: potassium silicate powder) after UV irradiation for 3 hours at T from - 100 to 150°C (curves 3<sub>irrad</sub> and 4<sub>irrad</sub>)

As can be seen, the behavior of the transmission (absorption) spectra does not depend on the composition of silicate powders. The spectra reveal a change in the percentage of transmission, but no specific changes (as in the case of diatomites) were observed. After UV radiation, a general decline in the peaks intensity was observed for the samples obtained from perlite using HTMW method.

#### **4. Discussion**

The research of optical properties of precursors for obtaining TRC has shown that transmission peaks of low intensity at 1.4-1.6  $\mu\text{m}$  are due to the presence of deformation vibrations of silicate bonds as a result of UV radiation. The peaks of average intensity at 1,6-1,8 $\mu\text{m}$  are also related to the structure of silicates. The peaks of high intensity at 1,3 $\mu\text{m}$  correspond to valence vibrations of crystal lattice  $\mu$  (Si-O-Si), whereas a small peak at 1,1 $\mu\text{m}$  is a result of deformation vibrations - (Si-O-Si) radiation defects. From the spectra it follows that UV irradiation leads to a decrease in the intensity of transmission bands, i.e. UV radiation contributes to a redistribution of the intensities responsible for defect formation in the crystal lattice and thus increases the radiation resistance of materials.

The observed maxima at 1.2 -1.6  $\mu\text{m}$  in the samples from the perlite rock are due to the presence of deformation vibrations of silicate bonds. As a result of UV radiation, violations of vibration bonds take place, and therefore a decrease in the intensity within the entire investigated transmission spectra is observed. A significant change in intensity (almost by a factor of two) is observed for the potassium silicate samples, presumably due to the structure. Potassium silicate has a crystalline structure. The structure of sodium samples has more amorphous phase. In this case UV irradiation should not affect the processes of intensity redistribution of deformation vibrations. The observed decrease in the intensity at 1.6-1.8 micron is associated with intrinsic structure of the initial silicates.

Measurements of the samples irradiated at low temperatures ( $-100^{\circ}\text{C}$ ) have shown that the intensity of silicate bond oscillations decreases because of the amplitude decrease due to "freezing" (in this case, the structure of spectra is preserved, as illustrate the figures for irradiated and non-irradiated samples).

At high temperatures ( $150^{\circ}\text{C}$ ), the picture is changed because under UV irradiation, a "radiation annealing" takes place that contributes to higher stability of certain structural disorders resulting in a relative increase of radiation-stimulated processes that promote increase in radiation resistance of materials.

#### **5. Conclusions**

The results of the research using UV irradiation show that a redistribution of the intensities of the crystal lattice vibrations  $\mu$ (Si-O-Si) takes place due to violations of valence bonds, as well as an increase in deformation vibrations, (Si-O-Si) defects as a result of irradiation, thus promoting an increase of the radiation-optical resistance of materials.

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