

Effect of Simulated Factors on Spectroscopic Characteristics of Materials for Thermoregulating Coatings

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Abstract. The paper presents some results of the research on the effect of 5 MeV electron irradiation on spectroscopic characteristics (optical and IR absorption, electrophysical parameters) of materials (sodium and potassium silicates) for thermoregulating coatings (TRC) obtained on the basis of rocks by hydrothermal-microwave method. It is shown that the electron irradiation promotes the formation of radiation-induced defects of different nature in the materials for TRC.

Keywords: electron irradiation, silicate, thermoregulating coatings, perlite, optical and infrared absorption, radiation defects

1. Introduction

The main trends of modern space instrument making industry are increase of space vehicle (SV) active lifetime to 10-15 years, improvements in leak integrity of their structure, wide use of new polymer composites. Therefore, of current concern is the application of physical modeling for comprehensive study of the behavior of SV materials under conditions of ground forced impact of the main factors of space environment such as streams of high-energy charged particles (electrons, protons, neutrons, etc.) [1-4].

It is known that as a result of irradiation with high-energy particles, point and cluster defects are formed. In irradiated material reflection coefficient decreases testifying the effects of radiation on the surface of thermal coatings. Apart from the near-surface defects, the scattering of charge carriers is also increased contributing to the changes in reflection coefficients of thermal coatings. Before the elastic impact with the thermal coating atoms, bombarding high-energy electrons lose a significant part of their energy by ionization, therefore the amount of defects (vacancies, interstitial atoms) after electron irradiation is much less than, for example after proton or neutron irradiation [3,4]. Also, in the case of electron irradiation, point defect concentration is greater than the concentration of complex radiation aggregates.

The study of structural defects in natural minerals is one of the most important tasks when investigating concentrating of raw materials at prospect evaluation survey.

There are several classes of structural defects caused by various reasons:

1) genetic defects arising in the process of mineral formation due to the introduction of isomorphous ions or the violations of the lattice structure, such as vacancies and

interstitials (Si and O). Most typical isomorphous impurities are Al, Ti, Ge, which are associated with the formation of different paramagnetic centers, depending on the compensator ion. This class also includes the O₂ centers that originate in the silicon-oxygen tetrahedrons with Si vacancy, as well as centers localized in the clusters of high-temperature β -phase of quartz;

2) radiation defects formed under the impact of natural radiation. These are primarily paramagnetic defects such as F-centers, i.e. oxygen vacancies captured electron, as well as a number of other defects with more complicated structure;

3) diffusion defects formed as a result of diffusion interaction of defects in minerals in natural conditions under the influence of natural radiation, temperature, etc.;

4) destruction defects that originate in the areas of high defectiveness, which relate to amorphisation processes, intergranular boundaries, accumulation of dislocations or interstitials, etc. This class covers a large number of defects, many of which may be complex aggregates.

Knowledge of the structural features and properties of silicate and other refractory compounds in crystalline, liquid, and glass-like form provides the possibility of purposive influencing their synthesis process and obtaining materials with predetermined performance characteristics.

The aim of this work is a comprehensive study of the spectroscopic characteristics of sodium and potassium silicates (obtained from perlite) for thermoregulating coatings subjected to irradiation with high-energy electrons.

2. Materials and methods

The characteristics of optical absorption (transmission) spectra of sodium and potassium silicates) obtained from perlite by hydrothermal-microwave method both initial and irradiated with 5 MeV electrons at a dose of 10^{16} electrons/cm²- in the near infrared region of the spectrum were studied. The irradiation was carried out using ELU-5 linear electron accelerator at 90 K in vacuum (10^{-5} Pa). The measurements of optical absorption (transmission) spectra were performed within the wavelength range from 1 μ m to 2.2 μ m.

Perlite is an acidic volcanic glass-rich rock. The raw material used in this study is perlite from Aragats deposits (Armenia) comprising the following basic components (in wt.%): SiO₂ - 73.7, Al₂O₃ - 13.58, Na₂O - 3.85, K₂O - 4.14, Fe₂O₃ - 0.82, MgO - 0.4, CaO - 0.8, ignition loss and water are 2.7 particles-size of less than 250 microns, bulk density of 2.4 g/cm³ [5].

Before the irradiation, the samples of sodium and potassium silicates, obtained by hydrothermal microwave (HTMW) processing of perlite, were dried in drying cabins until powdering. After electron 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, 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.

Dielectric permeability ϵ' of sodium metasilicate ($\text{Na}_2\text{SiO}_3 \cdot n\text{H}_2\text{O}$) was measured within the frequency range of 300 Hz - 1 MHz at room temperature. The used experimental device was based on the known bridge circuit and calibrated using BM 400G Tesla capacitance meter. Sinusoidal measuring voltage of 100 mV was applied to the sample, the measurement accuracy was ± 0.05 pF. The samples had a cylindrical shape with the following typical dimensions: 10mm in diameter and 3mm in height. The electrodes were made in the form of thin foils on the flat surfaces of the sample.

Elemental analysis of Na_2SiO_3 sample, performed by IR (FTIR) method in the frequency range of 4000-500 cm^{-1} using Nicolet 5700 spectrometer (ZnSe prism, Happ-Genzelapodization, corrected ATR distortion, 32 scans, resolution 4 cm^{-1}) has revealed 2.61% impurities including 1.45% of K_2O , 0.03% of chlorine, approximately 1.12% of potassium, zinc and zirconium oxides.

3. Results

1. Effect of electron irradiation on spectroscopic properties of sodium and potassium silicates, obtained by hydrothermal microwave (HTMW) processing of perlite. From our experimental results it follows that the non-irradiated samples (blue curves in the figures) reveal more complex structure (Fig. 1,2). The absorption spectra of sodium silicate samples clearly present intense absorption bands at $\lambda = 1.38 \mu\text{m}$ and $\lambda = 1.91 \mu\text{m}$ and a weak one at $\lambda = 1.2 \mu\text{m}$ (Fig. 1, blue curve). The potassium silicate samples on the contrary, reveal a weak absorption band at $\lambda = 1.38 \mu\text{m}$, but at the same time a new intense absorption band is presented at $\lambda = 1.5 \mu\text{m}$ (Fig.2, blue curve). Irradiation with electrons changes color of the samples from white to gray.

As can be seen from the figures, irradiation with fast electrons (red curves in the figures) leads to some changes in the sample structure and formation of new bands - defects as a result of both charge exchange of their own growth defects and violation of local regions in the crystal structure of the samples. In sodium silicate a new wide absorption band is manifested at $\lambda = 1.52 \mu\text{m}$ (Figure 1, red curve). In potassium silicate the intensive band at $\lambda = 1.5 \mu\text{m}$ completely disappears, but a new, not less intense absorption band appears at $\lambda = 1.3 \mu\text{m}$ (Figure 2, red curve).

The observed absorption band at $\lambda = 1.91 \mu\text{m}$ in sodium silicate is interpreted as a combination of valence and molecular vibrations of hydroxyl (OH) groups, the frequencies of vibrational fundamentals of which are in the far infrared region ($\sim 3500 \text{ cm}^{-1}$ and 1600 cm^{-1}). The nature of other absorption centers, including radiation damages in the crystalline structure (bands at $\lambda = 1.52 \mu\text{m}$ in irradiated sodium silicate and $\lambda = 1.3 \mu\text{m}$ in irradiated potassium silicate) requires an additional study using theoretical modeling of physical processes in disordered structures, such as "disorder-order".

The figures below also show the changes in transmission of irradiated samples relative to the non-irradiated ones (green curve).

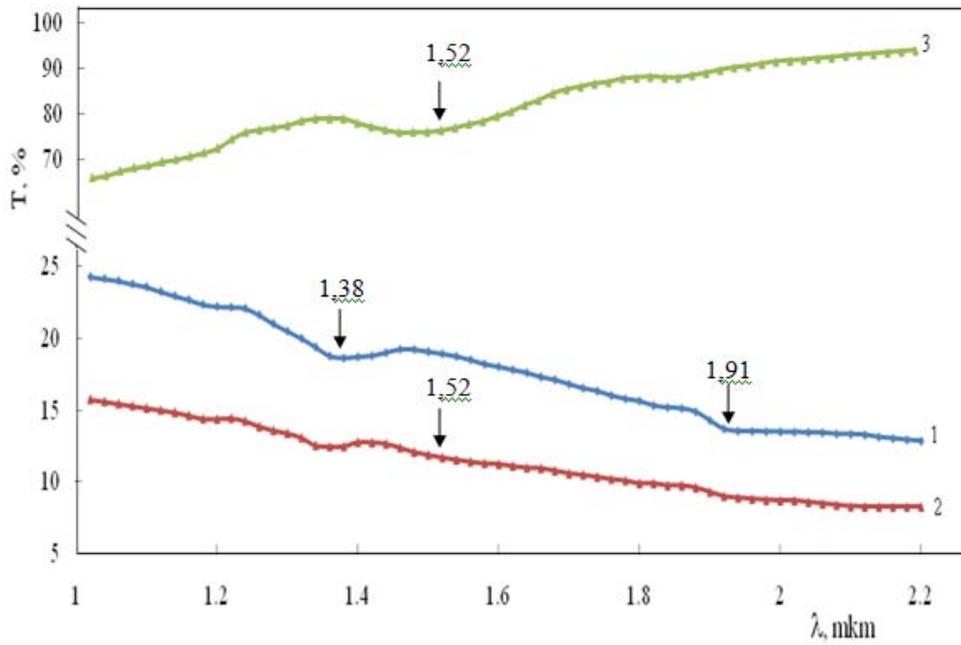


Fig.1. Sodium silicate sample.
 1- non-irradiated; 2- irradiated at a dose of 10^{16} electrons/cm²; 3- induced absorption: the absorption difference between irradiated and non-irradiated samples.

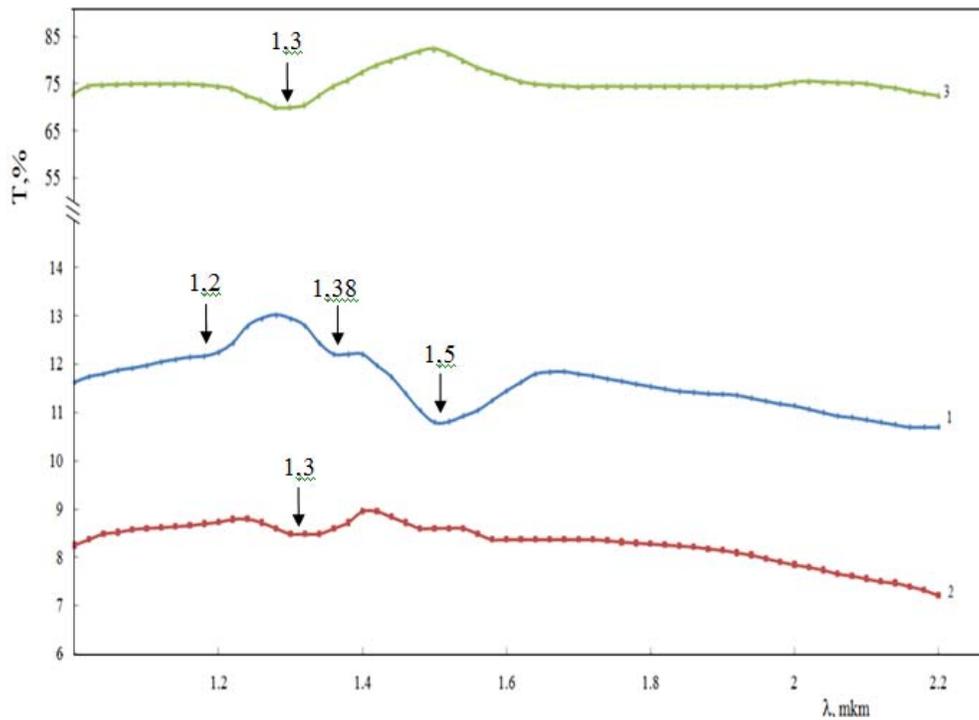


Fig.2. Potassium silicate sample.
 1- non-irradiated; 2- irradiated at a dose of 10^{16} electrons/cm²; 3- induced absorption: the absorption difference between irradiated and non-irradiated samples.

2. Dielectric permeability of sodium metasilicate irradiated with electrons

From the literature it is known that one of the important electrophysical parameters of materials is dielectric permittivity that allows estimating the losses and physical phenomena in the crystals under investigation, especially if they were subjected to external influences such as the radiation with fast electrons.

Figure 3 presents the experimental frequency dependences of the dielectric permittivity $\varepsilon'(f)$ of sodium metasilicate before and after irradiation with 5 MeV electrons. From the spectra it follows that the irradiation causes a significant reduction of dielectric constant ε' . This fact is particularly evident at low frequencies, when the dielectric constant is reduced more than 40 times. The observed change in the frequency dependence is probably due to the formation of radiation defects (point defects) under the influence of high-energy electrons that lead to the changes in the unit cell structure of sodium metasilicate.

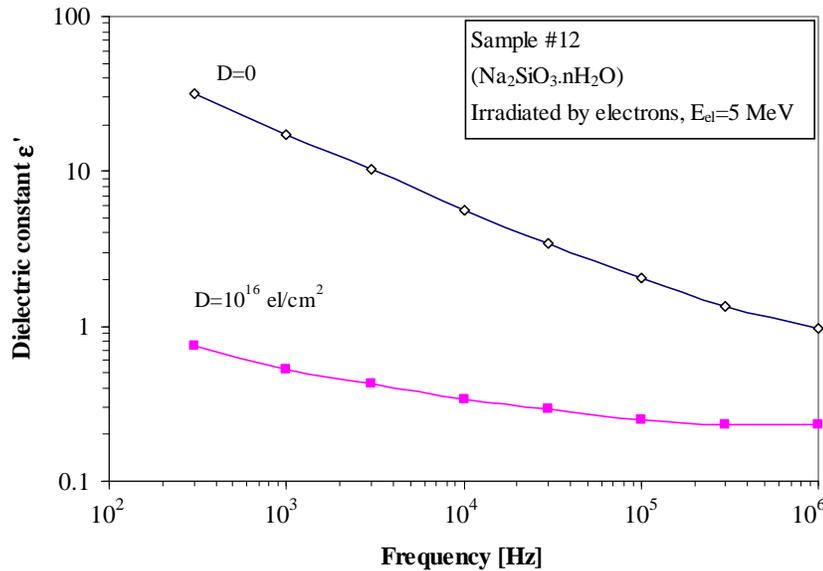


Fig.3. Frequency dependence of dielectric constant ε' of sodium silicate at 20°C before (D=0) and after (D=10¹⁶ el/cm²) irradiation with 5 MeV fast electrons.

3. Spectroscopic characteristics of materials for thermal coatings in infrared region

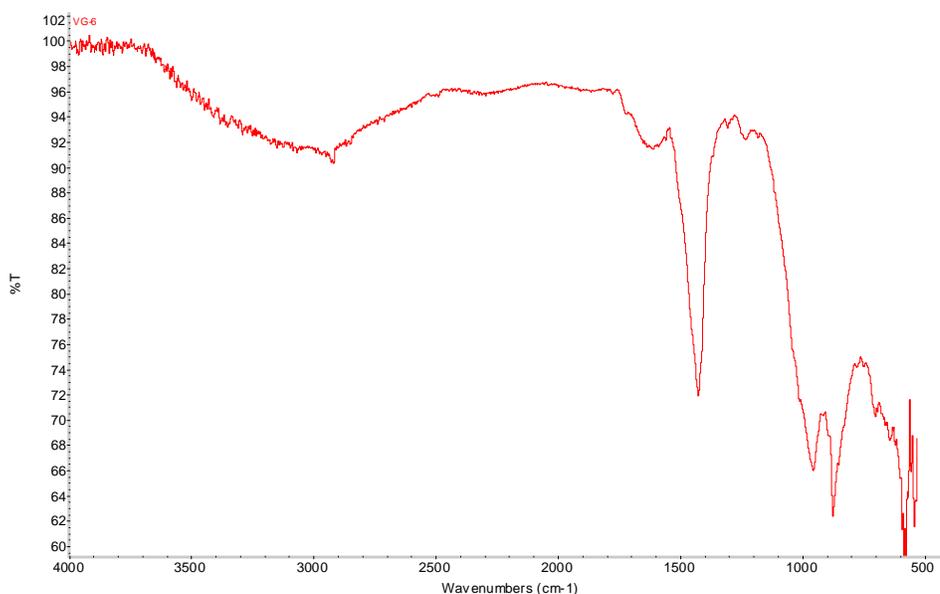
It is well known, the SV thermal regime depends on thermo-optical characteristics of coatings, in particular, the integral solar absorption factor A_s , the integral emission/absorption coefficient ε (emissivity factor) in the IR range.

Therefore, we investigated spectroscopic characteristics of sodium metasilicate samples within the spectral region of 500-4000 cm⁻¹ using: non-irradiated and irradiated with 5 MeV electrons at a dose of 10¹⁶ electrons/cm²

It is revealed from the X-ray diffraction analysis that the Na- silicate sample consists exclusively of the amorphous phase, whereas the K- silicate one presents well-defined crystalline phase.

It can be concluded from the results of X-ray diffraction analysis that the absorption capacity of coatings with amorphous structures is much higher than the absorption capacity of coatings having crystalline structure, which is especially important for the coatings of the same chemical composition.

Comparison of IR (the FTIR) absorption spectra of Na- silicate samples before and after irradiation (Fig. 4, 5) shows that these spectra are entirely identical at wave numbers within $700\text{-}4000\text{ cm}^{-1}$; some differences are observed at the wave numbers below 700 cm^{-1} which is outwardly demonstrates Figure 5.



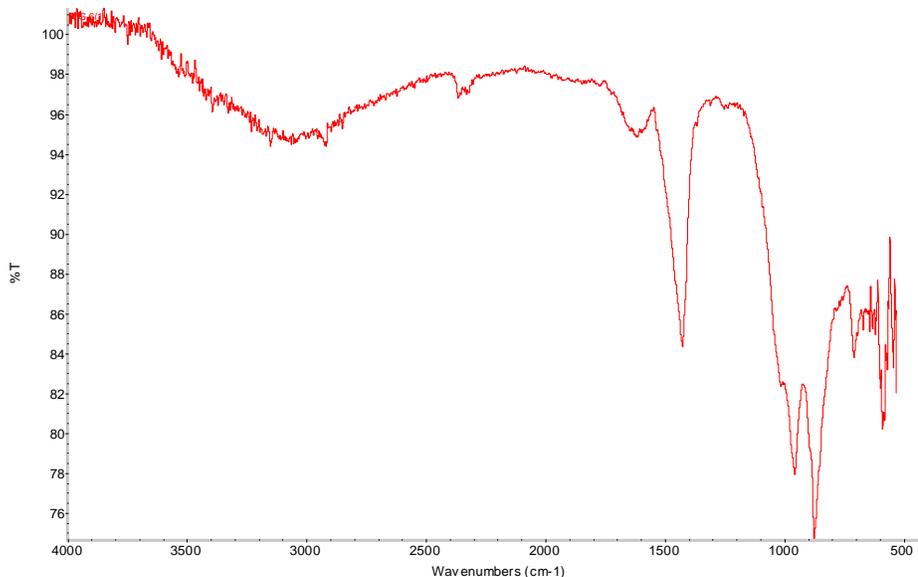
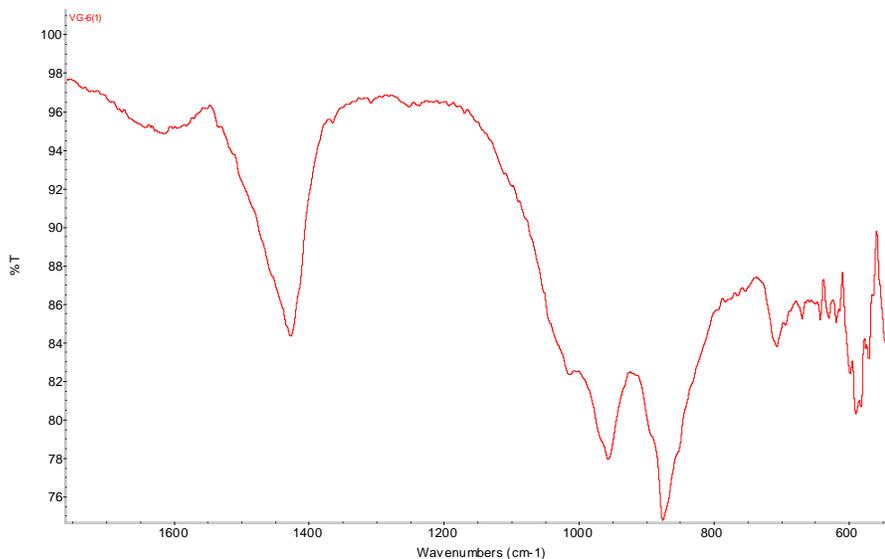


Fig.4. FTIR spectra (540-4000cm⁻¹) of Na₂SiO₃ sample before (VG-6) and after (VG-6¹) irradiation.

The ratio of the absorption bands for the samples in the registered IR spectra is taken on the basis of literature data [6-10], where the deformation vibrations of Me-O bonds (Me: metal atom) appear at 450-500cm⁻¹ and the valence vibrations of Me-O bonds in various inorganic glasses appear at 600-800 cm⁻¹



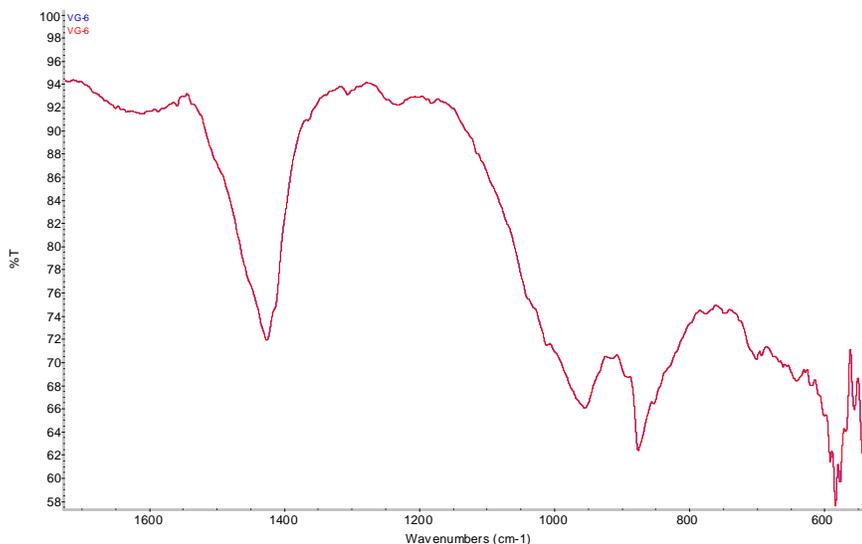


Fig.5. FTIR spectra (1700-4000 cm^{-1}) of Na_2SiO_3 sample before (VG - 6) and after (VG-6¹) irradiation.

According to [10], in particular, the deformation vibrations of Al -Si-O bonds are attributed to the absorption at 800 cm^{-1} . The shift of the absorption (about 3600-3400 cm^{-1}), characteristic of valence vibrations of OH groups, towards the lower wave numbers is explained by changes in the O-O bond lengths in the hydroxyl group. Consequently, the absorption at 3000 - 3200 cm^{-1} in the spectra of Na_2SiO_3 samples can be attributed to the presence of hydroxyl groups in the samples. Deformation vibrations of O-H groups are attributed to the absorption in the region of 1630-1645 cm^{-1} .

The absorptions in above regions also appear in the spectra of the samples studied (see Table 1).

Table 1

Assignments	Wave number (cm-1)			
	Na_2SiO_3 , before irradiation	Na_2SiO_3 , after irradiation	Perlite [1]	TAP*[1]
Si-O-Si symm.valencevib.	-	-	802	812
Si-O-Si asymm.valencevib.	-	-	1030	1192
-O-H bending vib.	1621	1616	1632	1628
-O-H valence vib.	-	-	3618	3579
O-H valence vib.	3064	3064		
Sodium carbonate (C-O)valence vib.	1424[2]	1424[2]		
Si-O-Si bending vib(δ)	955[3]	958[3]		

O-Si- O asymm. valence vib.	-	-		
M-O valence vib.v)	701[3]	706(669) [3]		
	643	642(629;618;598)	-	-
-	591	590	-	-
-	583	581	-	-
-	576	-	-	-
-	568	569	-	-
	556	-	-	-
	542	544	-	-

*-TAP- thermally activated perlite

4. Discussion

Thus, the results of experimental studies show that irradiation with 5 MeV fast electrons leads to structure changes and generates new bands, radiation defects as a result of both charge exchange of their own growth defects and violation of local regions in the crystal structure of the samples. In sodium samples, a new wide absorption band is manifested at $\lambda=1,52 \mu\text{m}$. In potassium silicate samples the intensive band at $\lambda=1,5 \mu\text{m}$ completely disappears, but a new, not less intense absorption band appears at $\lambda=1,3 \mu\text{m}$.

The observed absorption band at $\lambda = 1,91 \mu\text{m}$ in sodium silicate is interpreted as a combination of valence and molecular vibrations of hydroxyl (OH) groups, the frequencies of vibrational fundamentals of which lie in the far infrared region ($\sim 3500 \text{ cm}^{-1}$ and 1600 cm^{-1}).

The observed change of the dielectric parameters of frequency dependence is confirmed by the formation of radiation-induced defects: point defects under the influence of electrons that lead to structural changes of the unit cell structure of sodium metasilicate.

5. Conclusions

Thus, it can be concluded from the study of spectroscopic characteristics that electron irradiation results in a strong decrease of the transparency over the entire spectral region due to the formation of radiation-induced defects in structure of materials used for TRC synthesis; however, physical properties are maintained testifying to the radiation resistance of these materials.

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