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INFLUENCE OF IONIZING RADIATION ON THE DIFFUSE REFLECTION SPECTRA OF STEATITE CERAMICS SNC

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In this article, the radiation defects induced in steatite ceramics type- SNC- irradiated with high doses of gamma-rays of ^{60}Co source and mixed reactor n^0 -gamma-irradiation were studied using optical spectroscopy, i.e. diffuse reflection method. An analysis of the results of the diffuse reflection spectra showed that some structural defects are formed under gamma-irradiation. These are oxygen vacancies, unbound oxygen atoms, and E^1 - centers (a three-coordinated silicon atom that has captured an electron) in the ultraviolet region of the spectrum. In the visible region of the spectrum, the types of hole centers are different. After decomposing the spectrum of the visible region into Gaussians, it was found that in this region of the spectrum, with n^0 -gamma- irradiation of the reactor, in comparison with gamma-irradiation, various types of hole centers - (O-Me, Me-metal) are additionally formed. The efficiency of creating these structural defects in n^0 -gamma-reactor irradiated samples was higher compared to gamma irradiated samples.

Keywords: steatite ceramics type-SNC, diffuse reflection, gamma-rays, n^0 -gamma-irradiation, V-type hole centers.

Introduction

There is a growing need in the nuclear power industry for materials suitable for use in high radiation fields. In addition, there is the problem of effectiveness in using existing materials in extreme conditions. In this aspect, ceramic dielectrics have a special rank, including magnesian ceramics based on MgSiO_3 , i.e. steatite ceramics. Since in the future the main energy industry is connected with nuclear energy, its role is naturally great in nuclear and thermonuclear energy. In this industry, in some aspects, ceramics is an indispensable material and has been used for a long time. For example, ceramic products effectively work in the shell of a sealed zone of localization of an accident at a nuclear power plant under the conditions of complex exposure to decontaminating solutions and intense gamma radiation, as fire barriers in cable corridors, in the zone of increased radiation of a nuclear reactor at high temperatures, under conditions of powerful neutron fluxes, and other types of radiation. However, radiation processes in ceramic materials haven't been entirely studied in comparison with other dielectrics. Therefore, the study of radiation-stimulated processes in ceramic materials is relevant both from a scientific and application point of view.

The study of the effect of higher doses of γ -radiation on steatite ceramics SK-1 and SNCs showed that at higher doses of γ -radiation ($\geq 10^8$ R (8.8×10^7 Rad)) in these types of ceramics, structural defects with high thermal stability are formed [1-2]. The aim of this work is to study the nature of defects formed under the action of high doses of γ -radiation by the diffuse reflection (DR) method, as well as to compare them with n^0 - γ -irradiated samples of the nuclear reactor in steatite ceramics of the SNC types of ceramics compared to γ -irradiation.

1. Samples and experimental methods

Samples of ceramics of the SNCs type and, for comparison, SK-1 were studied as well. The ceramics are based on crystals of magnesium metasilicate- MgSiO_3 and glass of complex composition. The average grain size of crystals is 3-8 microns and occupies 60-70% of the volume of ceramics. The orthorhombic pyroxene enstatite (i.e. the crystalline phase magnesium metasilicate- MgSiO_3) belongs to the class of chain silicates. Its structure is well described on the basis of the concept of poling polyhedral: SiO_4 -tetrahedron and MgO_6 -octahedron (Fig. 1). SiO_4 tetrahedra are linked through common oxygen vertices into endless

zigzag chains $[\text{Si}_2\text{O}_6]_\infty$. Neighboring chains are not connected to each other and stretch in parallel, and in each individual chain the tetrahedra look either up or down, and in neighboring chains, the tetrahedra look in opposite directions. But the main core of the structure is zigzag chains of MgO_6 -octahedra connected by edges, which form odd floors of the overall structure. In even floors, $[\text{Si}_2\text{O}_6]_\infty$ chains are located, thus forming a single structure of the crystal phase of magnesium metasilicate MgSiO_3 [3].

The difference in these ceramics lies in the composition of the glass phases. Additionally, the following oxides CaO (0.52 wt%) ZnO (17 wt%) Na_2O (0.13 wt%) are present in the composition of the glass phase of SNC ceramics (Table 1). For 100%, the composition of the glass phase itself is taken, and not its relation to the composition of ceramics, see Table 1 [4,5]. The studied samples had dimensions of $10 \times 10 \times 1 \text{ mm}^3$, and the surface of the samples was subjected to polishing to achieve the same surface diffuseness. The samples were irradiated with γ -quanta of the ^{60}Co isotope ($E_{\text{av}\gamma} \approx 1.25 \text{ MeV}$), doses from 10^6 to $1.5 \times 10^{10} \text{ R}$ ($8.8 \times 10^5 \div 1.32 \times 10^{10} \text{ Rad}$), and neutrons in the channel of the WWR-SM reactor of the Institute of Nuclear Physics of the Academy of Sciences of the Republic of Uzbekistan with fluences $f \sim 10^{17} \div 10^{20} \text{ n/cm}^2$. The traditional optical method for studying color centers (CC) in crystals, based on the study of optical absorption (OA) spectra, is not suitable for most ceramic dielectrics, which strongly absorb and scatter light. Therefore, DR spectra, which in the general case are inversely proportional to the degree of absorption of the medium, can be used to estimate the absorption.

Table 1. The phase-mineralogical composition of steatite materials and chemical composition of glass according to [4]

Materials	Crystal phase (MgSiO_3)	Crystal phase	The composition of the glass phase (mass. %)							
			SiO_2	$\text{Al}_2\text{O}_3 + \text{TiO}_2$	Fe_2O_3	CaO	ZnO	BaO	Na_2O	K_2O
SNC	69.2	30.8	37.33	4.44	2.92	0.52	17.20	37.0	0.13	0.26
SK-1	71.6	28.4	39.46	3.49	2.68	-	-	54.26	-	0.11

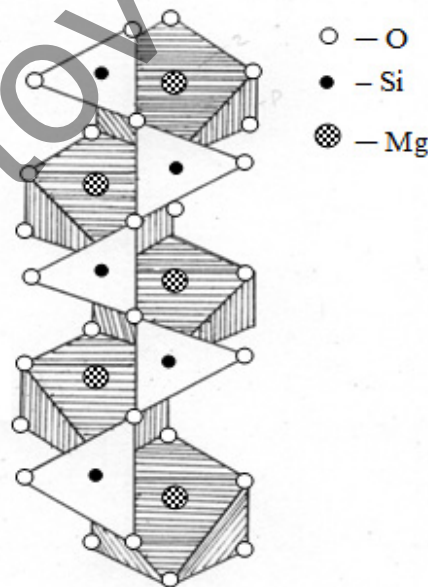


Fig. 1. Fragments of the structure of the crystal phase of the steatite ceramics of the SNC (the relationship between the metasilicate chain and the corresponding chain of cationic octahedra).

The DR spectra of ceramics were measured in the wavelength range of 200÷700 nm using a setup whose block diagram is shown in Fig.2. The degree of light reflection was evaluated by the reflection coefficient:

$$R = (I_{irr}/I_{unirr}) \cdot 100\%,$$

where I_{irr} and I_{unirr} – intensities of the reflected light from irradiated and unirradiated samples, correspondingly.

Unirradiated samples were used as references (with the same reflectance $\sim R$ as the research samples).

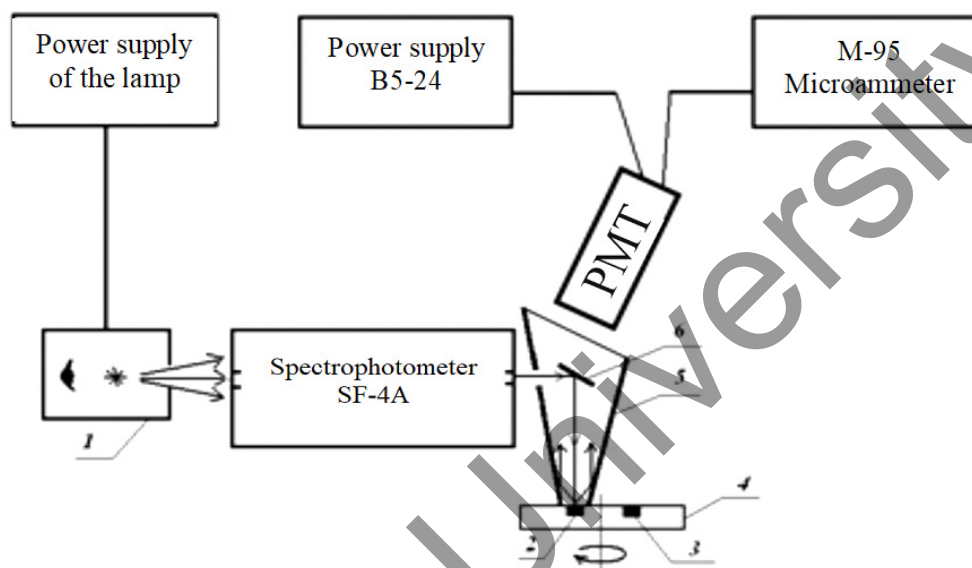


Fig.2. Scheme-of the setup for measuring DR spectra:

1-light source; 2-sample; 3-standard; 4-turn disc; 5-conical mirror; 6-swivel mirror.

When measuring DR spectra, the wavelength resolution of the SF-4A spectrophotometer was 0.1÷0.5 nm, and the error in determining the diffuse reflection coefficient was (R%) 3÷5%. The results obtained were averaged over three samples. When the absorption spectra were decomposed into Gaussians, the error was about 5%.

2. Results and discussion

The studied samples had a white color, and after γ -irradiation, they acquired a brown color, the color density increased with an increase in the dose of γ -irradiation. After γ -irradiation, the DR spectra show additional absorption bands (APB) in the UV region with maxima at $\lambda=220$ and 260 nm and a broad absorption band (AB) extending up to 700 nm with maxima at 400÷500. Intensities above the indicated AB increased with increasing dose of γ -irradiation (see Fig. 3, curves 1-3). It should be noted that this type of ceramics has not previously been studied by this method, with the exception of steatite ceramics SK-1 and high-alumina ceramics GB-7, UF-46. Therefore, to identify the detected absorption bands in the diffuse reflection (DR) spectra, we analyzed the literature data on silicates, silicate compounds and glasses, since the basis of this ceramics is the crystalline phase magnesium metasilicate- MgSiO_3 and silicate glass of complex composition (see tab.1). Literature data showed that color centers (CC), absorbing light in the region at $\lambda=220$ and 260 nm, were observed in quartz, quartz and silicate glasses when irradiated with ionizing radiation [6, 7].

They are associated with defects in the silicon-oxygen framework- SiO_2 . Since, in quartz glass and quartz, in the region of $\lambda=215$ nm the absorption is due to E^1 -center, which is caused by a three-coordinated silicon atom that captured an electron ($\equiv\text{Si}^{3+}$) and EPR signals with $g=2.00$, characteristic of E^1 -centers of various modifications. In the region of $\lambda=260\text{nm}$, the absorption is due to a non-bridging oxygen hole center

(NBOHC). It is known that in various types of silicates under γ -irradiation, EPR signals with $g = 2.00$ were observed, which are characteristic of E^1 - centers of various modifications. It should be noted that in all studied silicates, including quartz and silicate glasses, it is associated with the AB at $\lambda=215\div 230$ nm and the paramagnetic absorption signal with $g=2.00$. In our case, there are ABs at $\lambda=220$ nm and a paramagnetic absorption signal with $g=2.0012$, which we discovered in [8]. It can be assumed that the AB at $\lambda=220$ nm and the paramagnetic absorption signal with $g=2.0012$ is also associated with the same radiation defect, namely, with the E^1 - center.

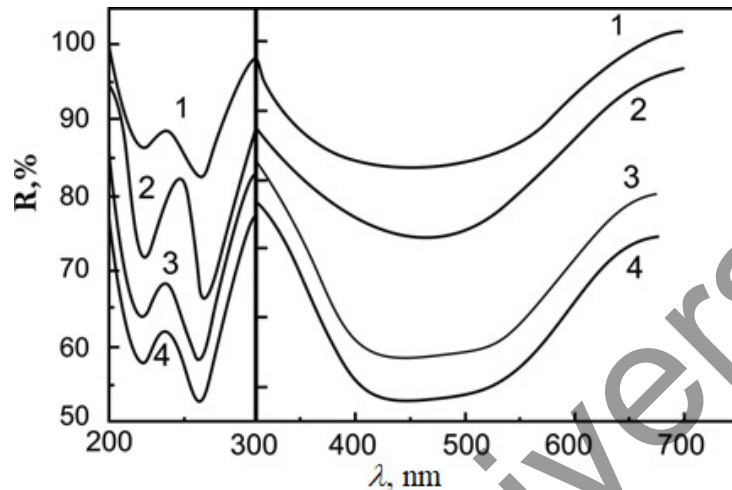


Fig.3. DR spectra of irradiated samples of SNC ceramics:
1- 2×10^6 R (1.76×10^6 Rad); 2- 10^9 R (8.8×10^8 Rad); 3- 1.5×10^{10} R (1.32×10^{10} Rad); 4- 10^{19} n/cm².

It is worth mentioning that in the above-mentioned work [8] in the samples under study in the initial state, one more signal of paramagnetic absorption with $g = 4.3$ was found in the low-field part of the spectrum. The color center that absorbs light at $\lambda=260$ nm could be NBOHC. Such a center is observed only in the absorption spectra (AS) of irradiated quartz glass or quartz after n° - γ irradiation [6,7]. A characteristic feature of NBOHC is the AB with maxima at $\lambda=260$ (4.75 eV), 620 (2 eV) nm and luminescence in the region at 660 nm (1.9 eV), which is observed both in the GL spectra and in the PL spectra ($\lambda_{\text{ex}}=260$ nm).

When excited in the $\lambda=260$ nm (4.75 eV) band of non-primary and irradiated ceramic samples, we did not detect luminescence in the region of 660 nm (1.9 eV), which is typical for NBOHC. It follows from here that the observed AB at $\lambda=260$ nm (4.75 eV) is not related to NBOHC. The following can be suggested about the nature of the AB with a maximum at $\lambda=260$ nm (4.75 eV): when analyzing the AS of oxides and silicate compounds with impurities of elements of the iron group, it was shown that in most compounds, for example, in MgO, Al₂O₃ and SiO₂ in the UV region AB can be caused by iron ions.

An analysis of the literature data showed that it is due to Fe³⁺ ions in tetrahedral coordination [6,7]. In silicates and oxides, iron ions can appear in the EPR spectra (electron paramagnetic resonance) both before and after irradiation with ionizing radiation. It is known that, depending on the synthesis conditions, iron ions can be present both in the form of Fe²⁺ and Fe³⁺. The Fe²⁺ ion has the 3d⁶ electronic configuration, while the Fe³⁺ ion has the 3d⁵ electronic configuration. The iron ion in the Fe²⁺ state does not give a paramagnetic absorption signal at temperatures above 77K [9,10], the Fe³⁺ ion has two paramagnetic absorption signals: with $g_1=4.3$, corresponding to iron ions in tetrahedral coordination, and a wide anisotropic EPR signal with $g_2=2.0026$ corresponding to octahedral coordination. The second signal corresponding to octahedral coordination was not revealed by us. This gives grounds to assume that the AB observed in the samples with a maximum at $\lambda=260$ nm, which occurs after γ -irradiation, is due to iron ions Fe³⁺ [9,10]. As mentioned above, after γ -irradiation in the visible region of the spectrum, a wide AB is observed with maxima at 400÷550 nm. Literature data on oxide and silicate compounds with ions of the iron group showed that they are associated with hole color centers (CC), which are due to the localization of holes on oxygen ions adjacent to cationic vacancies. In the presence of impurity ions of alkali, alkaline earth metals, or OH groups near the cation vacancy, the characteristics of such centers may change somewhat [11]. Hole-type color centers of various modifications (V-type centers) have wide AB in the visible region of the spectrum;

therefore, it can be assumed that the APB observed after γ -irradiation in the visible region can be due to V-type hole centers, which were also observed for SK-1 ceramics [12].

It is known that the specifics of the impact of reactor n° - γ -irradiation differs from γ -irradiation by the formation of many structural defects in their complexes, the displacement of atoms from the site of crystal lattices during elastic and inelastic interactions, etc. After n° - γ -irradiation of the reactor, similar ABs appear in the DR spectra, which were observed in γ -irradiated samples, but the intensity of the bands was higher compared to γ -irradiated samples (see Fig. 3, curve 4). The nature of the AB observed in the UV region of the spectrum with maxima at $\lambda=220$ and 260 nm has been discussed above. The study of difference DR spectra ($\Delta R=R_\gamma-R_{n^\circ\gamma}$) of γ - and n° - γ -irradiated samples showed that the spectrum is almost similar to the DR spectrum of ceramics SK-1 [12]. In the DR spectrum of n° - γ -irradiated samples, in contrast to the spectra of γ -irradiated samples, apart from the indicated AB, there are other ones. For example, a new AB appears in the UV region with a maximum of 248 nm. In γ -irradiated samples, this AB is not observed. In the visible region of the spectrum, ABs are observed with maxima at 400 and 450 nm, as well as a wide AB extending from 500 to 700 nm (Fig.3. curve4). An analysis of the literature has shown that AB with a maximum of 248 nm is observed in many silicates and quartz glasses. It is caused by an oxygen vacancy ($\equiv\text{Si}-\square-\text{Si}\equiv$). The formation of $\equiv\text{Si}-\square-\text{Si}\equiv$ can be due to the approaching of two E^1 -centers $\equiv\text{Si}^{3+}$ (switching the bond of two $\equiv\text{Si}^{3+}$) or direct kicking out of oxygen atoms during neutron irradiation. It can be seen from the figure (Fig. 3, curve 1) that both in the visible and near IR region of the spectrum, the picture is different. There are no obvious ABs here, except for the AB at 400 nm. However, in this region, one can see an overlap (superposition) of several ABs. Such color centers (CCs) are observed in many oxide compounds and complex oxide compounds as well. These can be -O-Me centers or a hole trapped by oxygen ions by an adjacent cationic vacancy. Hole-type color centers of various modifications (V-type centers) have wide ABs in the visible region of the spectrum; therefore, it can be assumed that the AB observed after γ -irradiation in the visible region can be due to V-type hole centers, which were also observed in SK-1 ceramics [12].

Probably, during γ -irradiation, the $\equiv\text{Si}-\text{O}-\text{Mg}$ bond is broken with the formation of $\equiv\text{Si}^{3+};\text{O}^-\text{Mg}$, that is, E^1 -centers and hole V-centers are formed. The absorption bands of hole V centers are observed in the range from 400 to 700 nm. In particular, they can be V^{2-} (O- ion near the cationic vacancy), V^- (cationic vacancy with one trapped hole), V^0 (cationic vacancy with two trapped holes). In the presence of impurities in oxides, the nature of hole centers also changes [11]. All of these centers, except for E^1 -centers, are essentially hole centers, which include the O⁻ ion located in a different environment. In order to separate each AB from the superposition, we decomposed the spectrum in the visible region into Gaussians. After decomposition, the spectrum turned out to be very similar to the decomposition spectrum for steatite ceramics SK-1 [12]. Considering the above mentioned, we also used the data for SNC ceramics. After decomposition into Gaussians, the identification of these centers showed that they consist of four types of V-centers with maxima at 389, 462, 542, and 618 nm (Fig. 4, curve. 2).

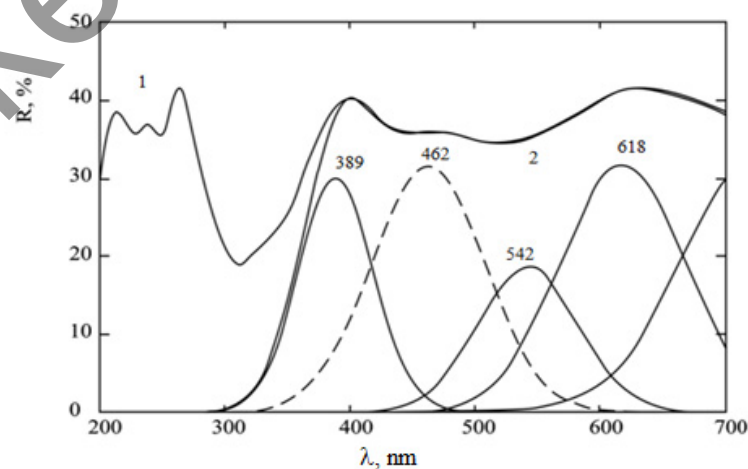


Fig.4. Difference diffuse reflectance spectra of γ - and n° - γ -irradiated SNC ceramics: ($\Delta R=R_\gamma-R_{n^\circ\gamma}$) (curve1) and their decomposition into Gaussians in the visible region of the spectrum (curve2)

The AB with a maximum at 618 nm is characteristic of NBOHC, which is an elementary intrinsic defect in silicate and quartz glasses. This band also appears in γ -irradiated images, but even at high doses ($\geq 10^9 \text{P}(8,8 \times 10^8 \text{Rad})$) its intensity is very weak. The creation of NBOHC may be due to the breaking of the $\equiv \text{Si-O-Me}$ bond with the removal of Me and the formation of the $\equiv \text{Si-O}^\cdot$ state. The efficiency of V-center formation in γ -irradiated images was very high compared to NBOHC. The AB with a maximum at 389 nm is associated with $-\text{O-Mg}$, (cationic vacancy in MgO) [11]. Due to the presence of crystalline (MgSiO_3) and glassy phases in the steatite ceramics of the SNC, and, consequently, the complex chemical composition [6,7], direct identification of the other two AB centers with maxima at 462 and 542 nm was difficult. However, probably, these ABs are also due to V-type hole centers and are associated with $-\text{O-Me}$ states. It is worth mentioning that the difference between the two ceramics lies in the composition of the glass phases, i.e., the presence of oxides such as ZnO (17.20%), CaO (0.52%) and Na_2O (0.13%) in the composition of the SNC glass phase. On the one hand, they are optically inactive elements, especially ZnO, CaO [13], their contribution to the DR spectra is not noticeable, Na_2O may favor the formation of NBOHC, but on the other hand, we do not exclude the contribution of these elements to the formation of (non-radiatively) hole centers in the form of $-\text{O-Me}$ (Me-metal, cation) in the visible region of the spectrum, which overlap against the background of intense AB lines, although after decomposing the total spectrum into Gaussians, it is impossible to distinguish them.

Conclusion

Thus, the effect of ionizing radiation on the reflective properties of the SNC steatite ceramics showed that, in contrast to γ -irradiation, the mixed n- γ -irradiation of the reactor additionally creates structural defects. These structural defects are of the type: oxygen vacancies $\equiv \text{Si}-\square-\text{Si}\equiv$, non-bridging oxygen hole center (NBOHC) $\equiv \text{Si-O}^\cdot$. An analysis of the decomposition of the DR spectra into Gaussians in the visible region of the spectrum showed that in the visible region of the spectrum, various hole centers of the type: $-\text{O-Me}$ (Me-metal, cation) are formed.

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