Investigation of radiation defects in steatite ceramics SK-1 and SNC by the EPR method

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The EPR spectra of γ- and n-γ-reactor irradiated steatite ceramics SK-1 and SNC has been studied. It is shown that structural defects of the E′-center type are created in the structure of the SK-1 and SNC ceramics under the action of high doses of γ-irradiation. After n-γ-irradiation and additional annealing, paramagnetic defect centers such as interstitial Me2++e− ions are created in the structure of the SNC ceramics, which are caused by amorphization of the ceramic crystal phase and the creation of a Mg enriched glass phase at the interface between crystalline and amorphous phases.

Keywords: steatite ceramics, radiation effects in ceramics, interphase boundary, structural defects in ceramics.

I. Introduction

Ceramic materials recommended themselves long ago as promising materials and are widely used in various fields of science and technology, including nuclear power in particular nuclear physics equipment due to their unique properties [1]. By radiation resistance, they concede only metals. Therefore, the interest in these materials is still tremendous. Compared with other dielectric materials, for example, single crystals and glasses, they are more stable, and are less time-consuming in production and manufacturing. As mentioned above, these materials are widely used in nuclear power engineering, for example, ceramics work efficiently in a shell of the sealed zone near location of nuclear power plants under the influence of complex action of deactivating solutions and intense γ-radiation, as fire barriers in cable corridors, in the active zone of an atomic reactor at high temperatures, in conditions of powerful neutron fluxes and other types of radiation. In this industry in some aspects, ceramics is an irreplaceable material and has been used for a long time [2].

Many parameters of ceramics, such as electrical con-
ductivity, bulk resistivity, dilatometric (TCLE-temperature coefficient of linear expansion) and mechanical properties in active radiation fields are important for the development of specific sites and are studied as a technical parameter. The use of ceramics as structural and electrically insulating material stimulated the work on the applicability of ceramics for specific purposes. All these require knowledge of the regularities of the processes taking place in the radiation field in structural materials. However, the radiation processes in ceramic materials are poorly studied in comparison with other dielectrics. Therefore, the study of radiation-stimulated processes in ceramic materials is relevant both from a scientific and a practical point of view as well. One of the most promising using in nuclear power engineering is magnesia ceramics based on MgSiO₃ so called steatite ceramics [3].

Steatite ceramic materials are also used as dielectrics in some devices exposed to ionizing radiation and are multiphase systems including crystalline and amorphous phases. In addition, steatite ceramics are used in the manufacture of integrated circuit packages, as well as insulating high-frequency material (bushing insulators, substrates, insulating rings). A characteristic feature of steatite ceramics in comparison with other ceramic materials is its high mechanical strength and low dielectric losses in some materials, for example, high-aluminous materials as GB-7, UV-46, multicorundum M-23 [3, 4]. In [5-8], we showed that in steatite ceramics SK-1, when exposed to high-dose γ-radiation (>10⁹ R), radiation defects with high thermal stability are formed, which are observed as peaks of thermo-luminescence (TL), EPR spectra (signal with \( g = 2.0012 \)) and diffuse reflectance spectra (DR) (\( \lambda = 220 \) nm). These defects are formed mainly in the crystalline phase of magnesium meta-silicate MgSiO₃ (non-stoichiometric MgSiO₃) or surface layers of grains of the crystalline phase with a defective structure formed.

The purpose of this work is to study, by using EPR method, the nature of radiation defects that are formed in steatite ceramics SK-1 and SNC under the influence of high-dose γ- and n-γ-reactor irradiation.

II. Research samples and experimental method

For investigation we used samples of ceramics of the types SK-1 and SNC, which have a fine crystalline homogeneous structure. The main phases of ceramics are crystals of magnesium meta-silicate MgSiO₃ and glasses of complex content. Crystals of magnesium meta-silicate have an average grain size of 3–8 µm and occupy 60–70% of the volume of the ceramic (see table) [3]. EPR measurements were performed on an ESP-300 spectrometer from Brucker (Germany), at a temperature of 300 K in a 3 cm range (operating frequency of 9 GHz). Measurements of g-factors were carried out by comparison with the EPR signal of a reference sample with Mn²⁺ (3-rd and 4-th lines), certified by Central Research Institute of Physical and Technical Measurements (VNIFTRI). When comparing the signals from the sample and the reference sample, we used a double rectangular resonator, ER-4105-DR, which makes it possible to measure the sample and the reference under absolutely identical experimental conditions. Samples with dimensions of 10×1×1 mm³ were used for the measurement. Gamma-irradiation of the samples was carried out by γ-quanta of the ⁶⁰Co isotope with an average energy of \( E_γ \approx 1.25 \) MeV at the dose rates of 10⁰–3500 R/s, doses from 10⁶ to 1.5×10¹⁰ R, at the channel temperature of \( \sim 303–343 \) K. The neutron irradiation was carried out in sealed quartz ampoules in the waterproof channel of the WWR-SM reactor, INP AS RUz at a temperature of 313–323 K and the thermal neutron fluence of 5×10¹³ n/cm² (the ratio of fast neutrons to thermal neutrons was 1:10), fluences 10¹⁷–10²⁰ n/cm².

The phase-mineralogical composition of steatite materials and the chemical content of glass according to [3, 4] are presented in the table.

<table>
<thead>
<tr>
<th>Materials</th>
<th>Phase-mineralogical composition (mass fraction, %)</th>
<th>Glassy phase content (mass fraction, %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SNC</td>
<td>Crystalline phase (MgSiO₃) 69.2</td>
<td>SiO₂ 37.33  Al₂O₃  4.44  Fe₂O₃  2.92  CaO  0.52  ZnO  17.20  BaO  37.0  Na₂O  0.13  K₂O  0.26</td>
</tr>
<tr>
<td>SK-1</td>
<td>Glassy phase 30.8</td>
<td>SiO₂ 39.46  Al₂O₃  3.49  Fe₂O₃  2.68  CaO  54.26  BaO  0.1</td>
</tr>
</tbody>
</table>

Table. Phase-mineralogical composition of steatite materials and the chemical content of glass.

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III. Results and discussion

In the initial state, one paramagnetic absorption signal with \( g=4.3 \) in the low-field part of the spectrum is observed in the EPR spectra of steatite ceramics SK-1 and SNC. No other signals of paramagnetic absorption were observed. Analysis of literature on oxides and silicate compounds [9-12] showed that the paramagnetic absorption signal with \( g=4.3 \) is observed in many iron-containing compounds, and it is due to iron ions (Fig. 1) in the \( \text{Fe}^{3+} \) state in tetrahedral coordination.

![EPR spectra of steatite ceramics SK-1 (a) and SNC (b).](image)

Figure 1. EPR spectra of steatite ceramics SK-1 (a) and SNC (b).

After \( \gamma \)-irradiation with a dose \( \sim 2 \times 10^6 \) R, along with a slight increase in the signal amplitude with \( g=4.3 \), one more paramagnetic absorption signal with \( g=2.0012 \) is observed in the mid-field part of the spectrum, the intensity of which increases without saturation even at exposure doses of \( 2 \times 10^{10} \) R (Fig. 1), which indicates the formation of structural defects in the ceramics SK-1 and SNC at high doses of \( \gamma \)-irradiation.

Based on the literature data on silicate compounds, quartz and silicate glasses, and taking into account the similarity of the shape of the line and the EPR parameters of the signal with \( g=2.0012 \) (H=5 G) observed in steatite ceramics SK-1 and SNC, we can conclude that this signal belongs to the \( E^- \)-center [5-8]. It was found that defect formation occurs mainly at the interface between crystalline (\( \text{MgSiO}_3 \)) and amorphous phases [5-8]. After reactor \( n-\gamma \)-irradiation, similar signals are also observed, and the intensity of the signals was greater than for the \( \gamma \)-irradiated samples (Fig. 2). No other signals were observed.

![EPR absorption signals with \( g=2.0012 \) at the samples of steatite ceramics SK-1 and SNC irradiated by \( \gamma \)-rays at the doses \( 2 \times 10^6 \) R (1), \( 2 \times 10^{10} \) R (2) and neutron fluences at \( 10^{19} \) n/cm\(^2\) (3).](image)

Figure 2. EPR absorption signals with \( g=2.0012 \) at the samples of steatite ceramics SK-1 and SNC irradiated by \( \gamma \)-rays at the doses \( 2 \times 10^6 \) R (1), \( 2 \times 10^{10} \) R (2) and neutron fluences at \( 10^{19} \) n/cm\(^2\) (3).

Investigation of the thermal stability of the EPR signal with \( g=2.0012 \) showed that in SK-1 ceramics it is annealed at a temperature of 773 K (500°C) and after additional \( \gamma \)-irradiation with a dose of \( 10^6 \) R it is annealed at temperatures \( \sim 1173-1273 \) K (900-1000°C). The reason for this difference is described in more detail in [4], therefore, we will not discuss this phenomena.

In contrast to the SK-1 ceramics, an additional paramagnetic absorption signal with \( g=1.99 \) appears at the "tale" of the signal with \( g=2.0012 \) in SNC ceramics annealed at a temperature of 773 K, after annealing and additional \( \gamma \)-irradiation at the dose of \( 10^6 \) R (Fig. 3 (b)).

![EPR spectra of steatite ceramics SK-1(a) and SNC (b) irradiated by neutron fluence \( 10^{19} \) n/cm\(^2\) with further annealing at the temperature 773 K and additional \( \gamma \)-irradiation at the dose 10^6 R.](image)

Figure 3. EPR spectra of steatite ceramics SK-1(a) and SNC (b) irradiated by neutron fluence \( 10^{19} \) n/cm\(^2\) with further annealing at the temperature 773 K and additional \( \gamma \)-irradiation at the dose 10^6 R.

In order to understand the reason for the appearance of the paramagnetic absorption signal with \( g=1.99 \), we investigated the glasses close to the glass phase of these ceramics. In the ceramic glass phases,
paramagnetic absorption signals with \( g = 1.99 \) were not detected even at doses of \( \sim 1.5 \times 10^{10} \) R. Consequently, it can be assumed that structural defects are formed mainly in the crystalline phase with disturbed stoichiometry. The EPR spectra of steatite ceramics have not been investigated by this method before, so it is expedient to involve data of other compounds with similar chemical composition. Analysis of literature data showed that a similar situation is observed in silicate glasses of the MeO-SiO\(_2\) system (Me-Mg, Ca). In silicate glasses, the content of alkaline earth oxide affects the resulting radiation defects detected by EPR. With an increase in the MgO (or CaO) content, a broad line appears with \( g = 1.97 \) [13-15]. Proceeding from this, it can be assumed that a metastable phase is formed on the thermal peaks of n-\( \gamma \)-irradiated ceramics, which during subsequent annealing turns into an amorphous phase, where EPR signals with \( g = 1.97 \) are produced with an additional \( \gamma \)-irradiation at a dose of \( 10^6 \) R. Apparently, amorphization occurs in the regions of phase separation of the crystalline phase of magnesium meta-silicate MgSiO\(_3\). As a result, a glass phase, enriched with Mg ions, is formed at the interfaces between the crystalline and glassy phases. On the other hand, it is known that the interval of sintering of steatite ceramics is very narrow, within 1543–1560°C (1816–1833 K) [3]. Therefore, slight deviations from the annealing regime can lead to a change in the chemical content, i.e. regions or local areas with disturbed stoichiometry can be formed. Chemical bonds at the interface boundaries are violated, so the interfaces become locations for accumulations of defects. These features can affect the response to the radiation during influence of radiation and temperature. It should be noted that due to the complex chemical composition of steatite ceramics [3, 4], the direct identification of the paramagnetic absorption signal with \( g = 1.99 \) by the optical method, i.e. the diffuse reflection (DR) spectrum was difficult. In the spectra of irradiated ceramics [6, 7], broad absorption bands (AB) were observed in the visible range of the spectrum, they were assumed to be related to V-type hole centers with disruption of the Si-O-Mg bond with the formation of \( \equiv \text{Si}^{3+}\text{-O}^{-}\text{-Mg} \) and \( \equiv \text{Si}^{-}\text{-O}^{-}\text{-Mg} \) bonds, it is also possible that this signal is also related to the V-type hole center \( \equiv \text{Si}^{3+}\text{-O}^{-}\text{-Me} \) (Me – alkaline earth metal) [13]. Literature data on alkaline-earth silicate glasses [13-15] of the system MeO-SiO\(_2\) (Me – Mg, Ca, Sr, Ba) showed that the defective paramagnetic centers \( g = 1.99 \) are characteristic of tetrahedra, in which the \( \text{Me}^{2+} \) ion left its normal position and moved into the interstitial space \( \text{Me}^{2+} \). This implies that in the SK-1 ceramics after n-\( \gamma \)-irradiation followed by annealing and additional \( \gamma \)-irradiation, there is mainly a breakdown of the siloxane bond according to the scheme: \( \equiv \text{Si}^{3+}\text{-O}^{-}\text{-Me} \) or \( \equiv \text{Si}^{-}\text{-O}^{-}\text{-Me} \), and in the SNC ceramics, in addition to the above-noted breaks in the siloxane bond, it is observed by the removal of \( \text{Me}^{2+} \) in interstitial space, with the capture of e, which is attributed to the electronic central interstitial cation characterized with \( g = 1.97 \). In addition, there is a possibility of the influence of the chemical composition of the ceramics on the above-mentioned processes, since there are no admixtures of Ca and Zn in the composition of the ceramic SK-1. At the same time, these impurities are present in the SNC ceramics and can be isovalently replacing the Mg atoms, forming a crystalline phase of the ceramic, with disturbed stoichiometry, increasing the MeO content in amorphous regions.

### III. Conclusion

Thus, under the action of large doses of \( \gamma \)-irradiation, structure defects of the E’-center type are created in the structure of the ceramics SK-1 and SNC. Under neutron irradiation and additional annealing followed by \( \gamma \)-irradiation, paramagnetic defect centers such as interstitial \( \text{Me}^{2+}+\text{e} \) ions are created in the structure of the SNC ceramics, which are caused by amorphization of the ceramic crystal phase and the creation of a Mg-enriched glass phase at the interfaces between crystalline and amorphous phases.

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