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

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Методом ЭПР спектроскопии исследованы спектры γ- и n^0-γ-реакторно облученных стеатитовых керамик СК-1 и СНЦ. Показано, что под действием больших доз γ-облучения в структуре керамик СК-1 и СНЦ создаются структурные дефекты типа E'-центров. После n^0-γ-реакторного облучения и дополнительного отжига с последующим γ-облучением в структуре керамик СНЦ создаются парамагнитные дефектные центры типа междоузельных ионов $Me^{2+}+e^-$, которые обусловлены аморфизацией кристаллофазы керамики и созданием обогащенной Mg стеклофазы на границах раздела кристаллических и аморфных фаз.

Ключевые слова: стеатитовая керамика, радиационные эффекты в керамике, граница раздела фаз, структурные дефекты в керамике.

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 $Me^{2+}+e^-$ 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 $MgSiO_3$ 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, mulitic-corundum M-23 [3, 4]. In [5-8], we showed that in steatite ceramics SK-1, when exposed to high-dose γ-radiation (>10^9 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) (λ=220 nm). These defects are formed mainly in the crystalline phase of magnesium meta-silicate $MgSiO_3$ (non-stoichiometric $MgSiO_3$) 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 $MgSiO_3$ 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 ESR signals from samples of a stable organic radical of diphenylpicrylhydrazyl (DPPH) and Mn^{2+} ions in Mg(Mn)O. The number of spins was determined by comparison with the EPR signal of a reference sample with Mn^{2+} (3-rd and 4-th lines), certified by Central Research Institute of Physical and Technical Measurements (VNIIFTRI). 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 $мм^3$ were used for the measurement. Gamma-irradiation of the samples was carried out by γ-quanta of the ^{60}Co isotope with an average energy of E_γ≈1.25 MeV at the dose rates of 100–3500 R/s, doses from 10^6 to 1.5×10^{10} R, at the channel temperature of ~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 5×10^{13} n/cm^2 (the ratio of fast neutrons to thermal neutrons was 1:10), fluences 10^{17}–10^{20} n/cm^2.

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

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

	Phase-mineralogical composition (mass fraction, %)		Glassy phase content (mass fraction, %)							
Materials	Crystalline phase ($MgSiO_3$)	Glassy phase	SiO_2	Al_2O_3+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		0.1

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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 Fe^{3+} state in tetrahedral coordination.

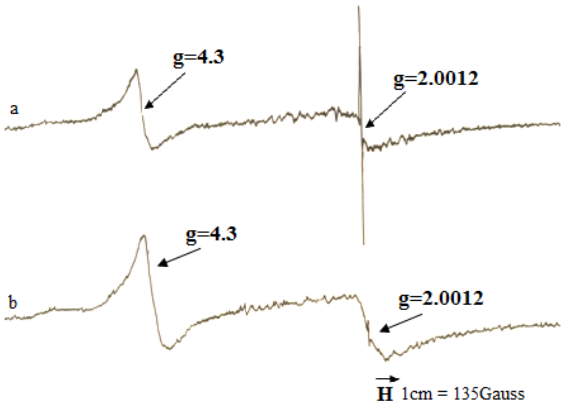


Figure 1. EPR spectra of steatite ceramics SK-1 (*a*) and SNC (*b*).

After γ-irradiation with a dose ~2×10^6 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 2×10^{10} R (Fig. 1), which indicates the formation of structural defects in the ceramics SK-1 and SNC at high doses of γ-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 ($MgSiO_3$) and amorphous phases [5-8]. After reactor n-γ-irradiation, similar signals are also observed, and the intensity of the signals was greater than for the γ-irradiated samples (Fig. 2). No other signals were observed.

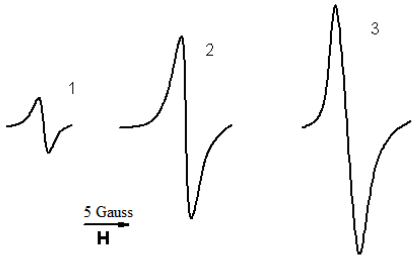


Figure 2. EPR absorption signals with g=2.0012 at the samples of steatite ceramics SK-1 and SNC irradiated by γ-rays at the doses 2×10^6 R (*1*), 2×10^{10} R (*2*) and neutron fluences at 10^{19} n/cm^2 (*3*).

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 (500ºC) and after additional γ-irradiation with a dose of 10^6 R it is annealed at temperatures ~1173–1273 K (900–1000ºC). 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 γ-irradiation at the dose of 10^6 R (Fig. 3 (b)).

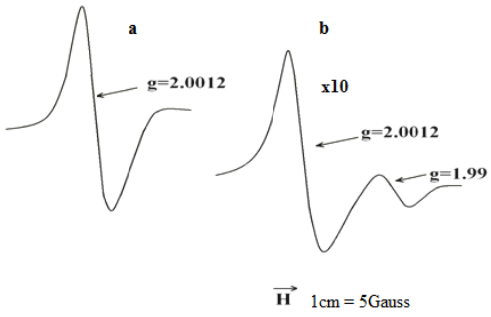


Figure 3. EPR spectra of steatite ceramics SK-1(*a*) and SNC (*b*) irradiated by neutron fluence 10^{19} n/cm^2 with further annealing at the temperature 773 K and additional γ-irradiation at the dose 10^6 R.

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,

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paramagnetic absorption signals with g=1.99 were not detected even at doses of ~1.5×10^{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-γ-irradiated ceramics, which during subsequent annealing turns into an amorphous phase, where EPR signals with g=1.97 are produced with an additional γ-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 $\equiv Si^{3+}$-O^--Mg and $\equiv$Si-O^--Mg bonds, it is also possible that this signal is also related to the V-type hole center $\equiv Si^{3+}$-O^--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 Me^{2+} ion left its normal position and moved into the interstitial space Me^{2+} e. This implies that in the SK-1 ceramics after n-γ-irradiation followed by annealing and additional γ-irradiation, there is mainly a breakdown of the siloxane bond according to the scheme: $\equiv Si^{3+}$-O^--Me or $\equiv$Si-O^--Me, and in the SNC ceramics, in addition to the above-noted breaks in the siloxane bond, it is observed by the removal of 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 γ-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 γ-irradiation, paramagnetic defect centers such as interstitial Me^{2+}+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.

References

[1] L. Thomé, S. Moll, A. Debelle, F. Garrido, G. Sattonnay, and J. Jagielski. Radiation Effects in Nuclear Ceramics. Advances in Materials Science and Engineering, **2012**, Article ID 905474, 13 pages (2012). https://doi.org/10.1155/2012/905474.

[2] N.S. Kostyukov, M.I. Muminov, S.M. Atrash, M.A. Mukhamedzhanov, N.V. Vasilyev. Dielectrics and radiation. Radiation conductivity. (Moscow, Nauka, 2001) [in Russian].

[3] V.G. Avetikov, E.I. Zinko. Magnesia electrotechnical ceramics. (Moscow, Energy, 1973) [in Russian].

[4] Yu.A. Brusnetsov, V.A. Pruchkin, I.S. Filatov. Marking of electronic equipment materials. TSTU Publishing (2006) [in Russian].

[5] É.M. Gasanov, K.G. Chan, K.K. Saidakhmedov. Action of a high dose of γ-rays on steatite ceramic. Atomic Energy **80**, No.2, 123-126 (1996). https://doi.org/10.1007/BF02414636

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[6] É.M. Gasanov, K.G. Chan, K.K. Saidakhmedov. Optical absorption spectra of irradiated steatite ceramic. Atomic Energy **85**, No.3, 258-260 (1998). https://doi.org/10.1007/BF02359345
[7] M.Z. Amonov, I. Nuritdinov, K.K. Saidakhmedov, et al. Diffuse reflection spectra of irradiated SK-1 ceramic. Atomic Energy **111**, No.4, 233-235 (2012). https://doi.org/10.1007/s10512-012-9492-y
[8] M.Kh. Ashurov, É.M. Gasanov, Kim Gen Chan, I Nuritdinov, K.Kh. Saidakhmedov. Luminescence of gamma-irradiated steatite ceramics. Inorganic materials **41**, No.2, 199-202 (2005). https://doi.org/10.1007/s10789-005-0044-x
[9] S.M. Brekhovskikh, V.A. Tyulnin. Radiation-induced centers in inorganic glasses (Moscow, Energoatomizdat, 1988) [in Russian]. https://inis.iaea.org/search/search.aspx?orig_q=RN:20027662
[10] O.N. Bilan, E.S. Voropai, S.M. Gorbachev et al. J. Appl. Spectrosc. **51**, 793 (1989). https://doi.org/10.1007/BF00659957
[11] S.V. Nemilov, A.A. Jilin. Spectrophotometric study of iron oxide in a glassy lead metasilicate in a wide temperature range. Inorganic Materials **10**, No.3, 513-517 (1974).
[12] Katsuhisa Tanaka, Kanchi Kamiya, Masaki Matsuoka, Toshinobu Yoko. ESR study of a sol-gel-derived amorphous Fe_2O_3-SiO_2 system. J. Non. Crys. Sol. **94**, 365-373 (1987). https://doi.org/10.1016/S0022-3093(87)80071-6
[13] V.A. Tyulnin, L.G. Gerasimova. Radiation-induced paramagnetic centers in liquation phases of glasses of system MgO-SiO_2. Inorganic Materials (Moscow) **9**, No.8, 1463-1465 (1973) [in Russian].
[14] V.A. Tyulnin. Structure of glasses of system MgO-SiO_2SiO_2 and CaO-SiO_2 according to the research results of radiation-induced color centers in them. Inorganic materials **7**, No.12, 2234-2239 (1971) [in Russian].
[15] V.A. Tyulnin. Investigations of radiation-induced paramagnetic and optical absorption in glasses of system SrO-SiO_2 and BaO-SiO_2. Inorganic materials **8**, No.1, 152-155 (1971) [in Russian].

ЭПР услуби ёрдамида СК-1 ва СНЦ стеатит керамикаларида радиациявий нуқсонлар ҳосил бўлишини ўрганиш

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ЭПР спектроскопия услуби ёрдамида СК-1 ва СНЦ керамикаларда γ- ва n^0-γ-реактор нурланиши таъсиридаги спектрлари ўрганилди. Юқори дозали γ-нурланишда СК-1 ва СНЦ керамикалар структурасида E'-типидаги нуқсонлар ҳосил бўлиши кўрсатилди. n^0-γ-реактор нурланиши ва қўшимча куйдиришдан кейин γ-нурлантиришда СНЦ керамика структурасида тугунлараро $Me^{2+}+e^-$ ионлари типидаги парамагнит нуқсонлар ҳосил бўлиб, улар керамика кристалл фазаси аморфизацияси ва кристал ва аморф чегарасида тўйинтирилган. Mg шиша фазаси ҳосил бўлиши билан асосланади.

Калит сўзлар: стеатит керамикалар, радиациявий нурланиши таъсири, структуравий нуқсонлар

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