

Radiation-induced paramagnetic centers in Bioglass[®]

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The X-band ($\nu = 9.4$ GHz) electron spin resonance (ESR) and thermally stimulated luminescence (TSL) spectra of the UV-, X-, and γ -irradiated Bioglas[®] samples of different composition (Bioglass[®] I and Bioglass[®] II) have been investigated. The efficiency of generation of electron and hole centers strongly depends on basic Bioglass[®] composition and is almost independent of ionizing radiation type and presence of Fe^{3+} non-controlled impurity in the glass network. The spin Hamiltonian parameters (g and a values) and thermal stability of the radiation-induced centers have been evaluated. The results of TSL measurements show good agreement with ESR data. Energetic structure, formation peculiarities and specific models of the radiation-induced paramagnetic centers in the Bioglass[®] network are discussed.

1. Introduction

The alkali silicate phosphate glasses of $\text{SiO}_2\text{-Na}_2\text{O-CaO-P}_2\text{O}_5$ system are intended to be used in the human body as an implant material and become attached to living tissue. These glasses are called bioactive and contain less than about 60 wt% SiO_2 . The chemical composition of bioactive glasses is similar to composition of the bones. A bone is composed in 1/3 of the organic materials and in 2/3 of the inorganic materials and water. The inorganic part of the bone is composed of calcium phosphate (crystalline hydroxyapatite (HAP) and non-crystalline calcium orthophosphate), calcium carbonate and small amount of magnesium oxide dopant. Since the discovery of Bioglass[®] [1], various kinds of glasses and glass ceramics [2]–[4] have been found to bond to living bone. Bioglass[®] surface, which can induce the

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formation of an apatite layer *in vivo*, or is pre-coated with an apatite layer, will demonstrate good bone-bonding properties [5]–[7].

The ESR spectroscopy proves to be a powerful method for studying bioactive materials. As paramagnetic probes for such studies one can use impurity ions of transition metals and radiation-induced centers which could trap electrons and holes on different sites of glass network. At present impurity paramagnetic ions and radiation defects are widely studied in phosphate glasses of different composition. Particularly, the radiation-induced PO_4^{2-} hole centers in the alkali and alkali earth phosphate glasses, characterized by ESR hyperfine doublet from ^{31}P isotope (nuclear spin $I = 1/2$) were studied by different authors [8]–[10]. Different models have been proposed for the symmetry of the PO_4^{2-} radical (anisotropy of g tensor) and localization of unpaired spin in the glass network.

On the other hand, only several papers report on the ESR study of the radiation-induced defects in hydroxyapatites [11]–[14]. Particularly, the F^+ centers were observed in carbonated HAP [13]. In plasma-sprayed and β - and γ -irradiated HAP the anisotropic ESR signal related to O^- anion-radicals adjacent to a calcium vacancy, [14], was registered.

2. Experimental details

2.1. Preparation and characterization of Bioglass[®] samples

The investigation was carried out using two types of Bioglass[®] produced by Jelenia Góra Optical Factory (Poland) [1], with their compositions being as follows (in wt%):

- 1) 45 SiO_2 :24.5 Na_2O :24.5 CaO :6 P_2O_5 (Bioglass[®], BG I or 45S5),
- 2) 46 SiO_2 :25.5 Na_2O :24.5 CaO :4 P_2O_5 (Bioglass[®] II or BG II).

The as-synthesized Bioglass[®] samples were submitted to treatment by the following physiological solutions: 0.9% NaCl and SBF (simulated body fluid) with $\text{pH} = 7.4$ for 2 hours. The SBF contains the inorganic ions of concentrations close to those in blood plasma [4], [15]. As was verified by SEM and EDAX spectra [16], that exposure to 0.9% NaCl solution on BG samples caused the formation of areas enriched with calcium and poor in silica.

2.2. ESR measurements

The X-band ESR measurements were carried out at room temperature using a RADIOPAN SE/X-2544 (Poznań, Poland) and AE-4700 (Lviv, Ukraine) commercial computer controlled spectrometers, operating in the high-frequency (100 kHz) modulation mode of magnetic field. The parameters of the spectra were evaluated using a BRUKER simulation program "SimFonia". Microwave frequency was controlled by diphenylpicrylhydrazyl (DPPH) g -marker ($g = 2.0036 \pm 0.0001$). The intensity of ESR spectra was evaluated according to a special standard ($N = 5 \times 10^{15}$ spins/G). The UV-irradiation of samples was carried out at room temperature using a lamp of the DKsEL-2000 type. The X-irradiation was carried

out with the use of an URS-55A standard apparatus (Cu K_{α} radiation, $U = 40$ kV, $I = 10$ mA). The exposition time was equal to 60 min.

2.3. TSL measurements

Thermally stimulated luminescence was registered in a Riso automated reader TL/OSL-DA-12. The irradiation of samples was performed with a 40 mCi Sr^{90} γ -source. The irradiated dose was equal to 2 Gy. In order to detect the thermally stimulated processes, the emission signal was registered while samples were heated at a linear rate of 3 °C/s.

3. Results and discussion

3.1. ESR spectra of the irradiated Bioglass®

For all as-synthesized Bioglass® samples a small quantity of iron impurity yields the broad ESR signal at $g_{\text{eff}} \approx 4.29$ and $g_{\text{eff}} \approx 2.00$ (Fig. 1) typical of vitreous (or glassy) state. These signals have been registered in a number of glasses of different composition [17]–[19] and are assigned to the isolated Fe^{3+} ($3d^5$, ${}^6S_{5/2}$) ions on the tetrahedrally coordinated sites with strong rhombic distortion ($g_{\text{eff}} \approx 4.29$) and on the sites nearly cubic local symmetry ($g_{\text{eff}} \approx 2.00$), [17], [20], [21]. The intensity of the Fe^{3+} ESR spectra in BG I is 5–10 times greater than that in BG II ones. The total amount of the Fe^{3+} ions in the samples under investigation estimated by ESR does not exceed 10^{-2} wt%.

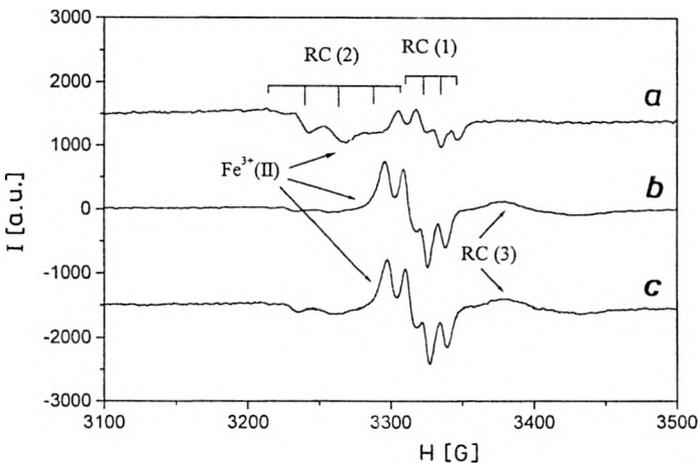


Fig. 1. The X-band EPR spectra of UV-irradiated Bioglass® I registered at $T = 300$ K in the as-synthesized (a), pretreated in NaCl solution (b) and SBF (c) samples.

The ESR spectra presented in Figs. 1 and 2 are visible against the background of the width iron line. The UV- and X-irradiation of BG I samples at room temperature leads to generation of stable paramagnetic centers of three types designated as RC (1), RC (2) and RC (3), Fig. 1. The UV- and X-irradiation of BG II samples causes

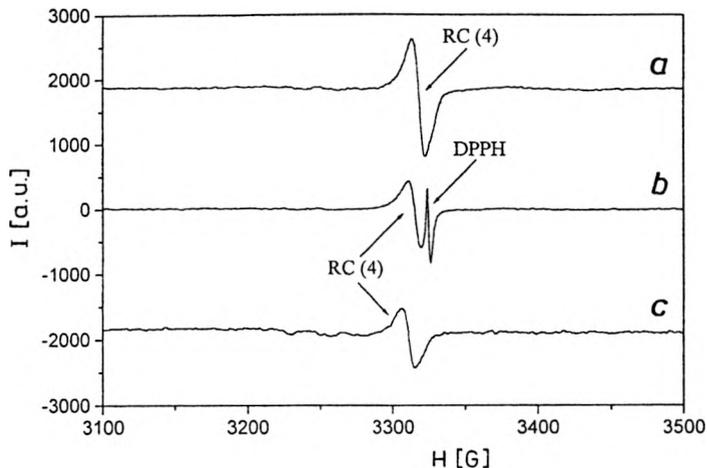


Fig. 2. The X-band EPR spectra of the Bioglass® II registered at $T = 300$ K in UV-irradiated and pretreated in the SBF (a), X-irradiated as-synthesized (b), and pre-treated in NaCl solution (c) samples.

generation of an additional stable RC (4) center, Fig. 2. These were also observed weak ESR signals of the RC (2) and RC (3) centers in the BG II sample. The efficiency of generation of centers of different types strongly depends on basic glass composition. Particularly, a small increase of SiO_2 and Na_2O content and a decrease of P_2O_5 content in the glass composition results in increasing amount of the RC (4) center and in a strong decrease of the amount of RC (1), RC (2) and RC (3) centers, and *vice versa*. As a result the RC (4) centers were observed in BG II, whereas RC (1), RC (2) and RC (3) centers were observed in the BG I (Figs. 1 and 2). Pre-treatment of the BG I samples in the NaCl solution and SBF leads to a decrease of the amount of RC (2) centers and an increase of the amount of RC (3) centers, whereas the amount and type of radiation-induced centers in the BG II only slightly depend on pre-treatment of the samples (Figs. 1, 2). The types of centers are independent of the kind of ionizing irradiation (UV, X and γ). Also the intensity of the ESR spectra of Fe^{3+} (I) and Fe^{3+} (II) centers in the irradiated BG I and BG II samples does not change.

The ESR spectrum of RC (1) centers is characterized by effective g value of the hole type ($g_{\text{eff}} > g_e = 2.0023$) and consists of four equidistant lines with the integrated intensity ratio close to 1:3:3:1 (Fig. 1). This signal could be explained assuming the superhyperfine (SHF) interaction of unpaired electron of the spin $S = 1/2$ with the magnetic moment of one nearest nucleus with nuclear spin $I = 3/2$ or three nearest nuclei with the spin $I = 1/2$. Since the number of components in the SHF structure $N = (2nI + 1) = 4$ the number of equivalent nuclei can be $n = 1$ or $n = 3$. The analysis of the isotopic composition of elements occurring in Bioglass® shows that it is either a single nucleus of the ^{23}Na isotope ($I = 3/2$, natural abundance 100%) or three nuclei of the ^{31}P isotope ($I = 1/2$, natural abundance 100%) that are the sources of SHF interaction.

The ESR spectrum of the RC (2) center is characterized by approximately isotropic hole-like g -factor and consists of five approximately equidistant lines of the intensity ratio close to 1:4:6:4:1, which can be ascribed to ^{31}P isotope superhyperfine structure. The fivefold SHF splitting of the ESR spectra of RC (2) center is caused by interaction of an unpaired spin with four nearest nuclei of the ^{31}P isotope ($N = 5$ for $I = 1/2$ and $n = 4$). The ESR spectrum of RC (3) center is characterized by weakly resolved broad line ($\Delta H_{pp} \approx 50$ G) with g -factor of electron type ($g_{\text{eff}} < g_e = 2.0023$). The ESR spectrum of RC (4) center consists of asymmetric line ($\Delta H_{pp} \approx 9$ G) with a hole-like g -factor. All spectra of the radiation-induced centers are independent of temperature in a range from 77 K to room temperature.

The lines related to the RC (1) center completely vanish at 230 °C, whereas the intensity of ESR spectrum of the RC (2) center does not change after heating up to $T > 280$ °C. The RC (3) related lines disappear at 280 °C, whereas the RC (4) related lines disappear at 200 °C [22].

3.2 ESR parameters and models of radiation-induced centers in Bioglass®

For identification of radiation-induced centers the parameters of ESR spectra were evaluated and analyzed. The ESR spectra of radiation-induced centers can be described by spin Hamiltonian in the following general form:

$$\mathcal{H} = \beta \mathbf{H} \cdot \mathbf{g} \cdot \mathbf{S} + \mathbf{I} \cdot \mathbf{a} \cdot \mathbf{S} \quad (1)$$

where β is the Bohr magneton, a and g are the tensors of magnetic superhyperfine interaction between the electron of spin S and a nuclei of spin I , and electronic Zeeman interaction, respectively. In the case of axial symmetry when axes of the tensors g and a are coincident the spin Hamiltonian (1) can be rewritten in the form

$$\mathcal{H} = \beta [g_{\parallel} S_z H_z + g_{\perp} (S_x H_x + S_y H_y)] + a_{\parallel} S_z I_z + a_{\perp} (S_x I_x + S_y I_y) \quad (2)$$

where $g_{\parallel} = g_{zz}$, $g_{\perp} = g_{xx} = g_{yy}$, $a_{\parallel} = a_{zz}$, $a_{\perp} = a_{xx} = a_{yy}$.

The g - and a -values for the radiation-induced paramagnetic centers in Bioglass® obtained in isotropic SHF interaction approximation are presented in the Table.

Table. The spin Hamiltonian parameters obtained as the best fit of the experimental (room temperature) and simulated ESR spectra and TSL peak of radiation-induced centers.

Center number	TSL peak [°C]	g values		a values		Type of centers
		g_{\parallel}	g_{\perp}	a_{\parallel}, G	a_{\perp}, G	
RC (1)	110	2.009 ± 0.001	2.005 ± 0.001	12 ± 1	12 ± 1	hole
RC (2)	440	2.048 ± 0.001	2.048 ± 0.001	23 ± 2	23 ± 2	hole
RC (3)	—	1.965 ± 0.005	1.953 ± 0.005	—	—	electron
RC (4)	110	2.009 ± 0.001	2.005 ± 0.001	—	—	hole

It should be noted that in silicate glasses scission of the chemical bonding creates many defect centers. Specifically, breaking the Si–O bond creates the non-bridging oxygen hole center as follows:



Bioglass[®] contains two glass-forming components. Usually, in oxide glasses and crystalline compounds silicon is fourfold oxygen-coordinates. However, the presence of phosphorus can force the silicon to a higher coordination. One considers various models describing the mixed silicate-phosphate glasses:

- 1) incorporation of silicon-oxygen polyhedra into or between the $[\text{PO}_4]$ tetrahedra chain,
- 2) formation of separate structural elements containing $[\text{SiO}_4]$ tetrahedra by phase separation, *etc.*

On the basis of the presented ESR and literature data we can conclude that the RC(1) and RC(4) centers can be described in the framework of HC_2 [23] and O^- [24] center models, which have been proposed for the alkali silicate glasses with great amount of alkali modifiers. In accordance with these models the RC (4) center is a hole captures at the Si-O tetrahedron, which has 3 non-bridging oxygen, and the wave function of the hole presumably largely restricted to the 3 non-bridging oxygen [22]. The RC (1) center is the O^- localized nearest to the Na^+ ion. It is the so-called L-center, $(\text{Si}-\text{O}^--\text{Na}^+)$ [25], where the four-line superhyperfine structure observed in their ESR spectrum is caused by one ^{23}Na nucleus. The RC(2) center can be interpreted as an electron, trapped at oxygen vacancy. The SHF structure of RC (2) centers could be explained by the interaction of an electron with four nearest ^{31}P nuclei of the glass network. The RC(2) centers in Bioglass[®] are characterized by high thermal stability and have no analogies in literature.

The RC (3) electron centers cannot be assigned to the well-known centers of the E' type. The nature and electron structure of these centers need additional study by means of ESR and other spectroscopic method.

3.3. TSL results

The TSL glow curves for unirradiated Bioglass[®] samples did not show any TSL signals. Typical glow curves for both types of γ -irradiated Bioglass[®] (BG I and BG II) are presented in Fig. 3. For both types of the glass the first maximum has been observed at about 100–110 °C, whereas the second one at about 150–160 °C, for BG I type of glass only. For the two types high-temperature maximum was at 420–440 °C. The high-temperature maximum is approximately 20 times higher than the low-temperature maxima. After the preheating of samples to 600 °C the high-temperature maximum completely disappears. After pre-heating up to 300 °C the maximum at about 110 °C disappears in both types of glasses and the BG I samples show the 150–160 °C peak, exclusively.

One relates the TSL measurements to the ESR data. Particularly, the TSL glow peaks at 100–110 °C, 150–160 °C, and 420–440 °C can be assigned to the RC (4), RC (1) and RC (2) centers, respectively.

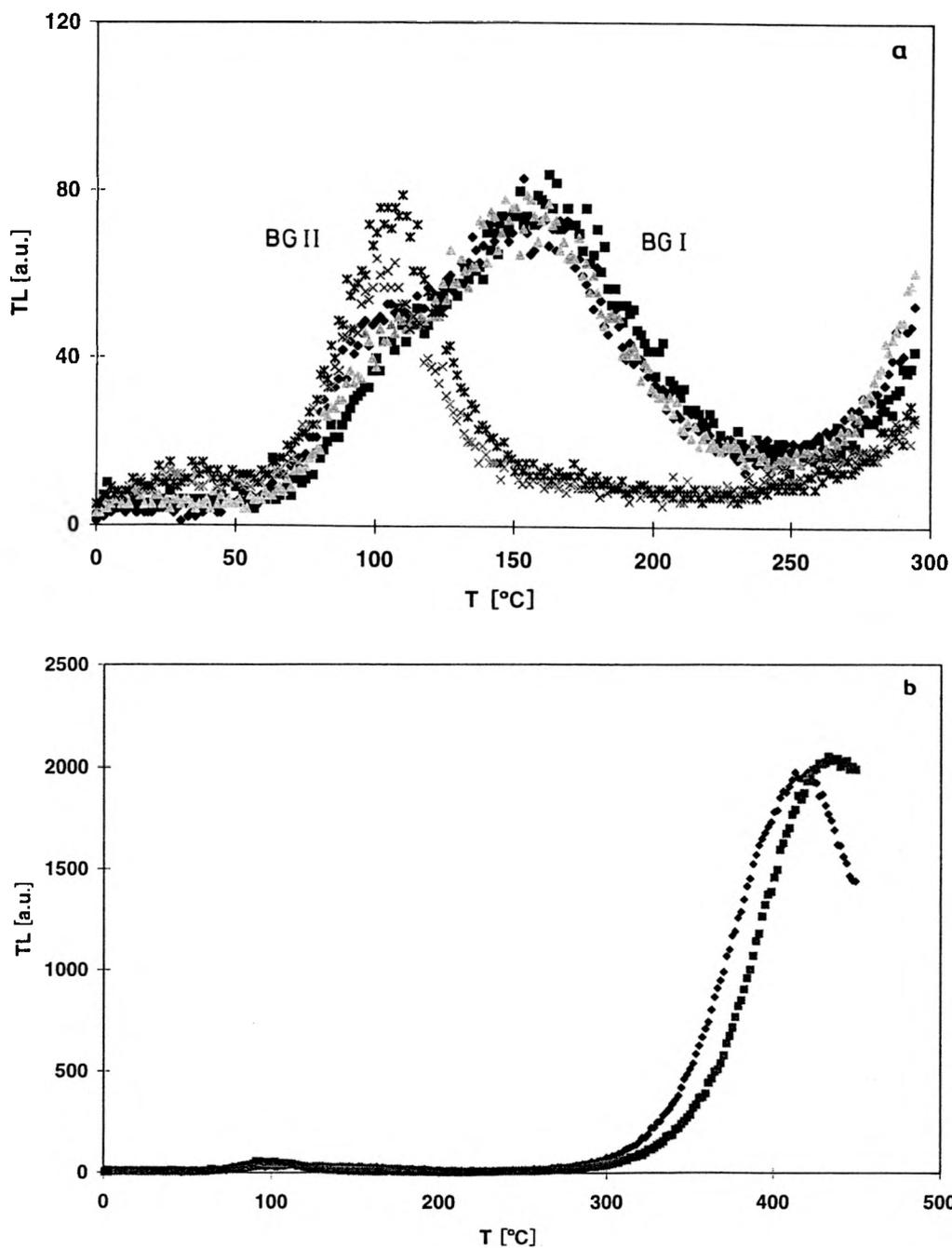


Fig. 3. The TSL glow curves of the three Bioglass[®] I (BG I) and two Bioglass[®] II (BG II) samples registered in the temperature range of 20–300 °C (a) and 20–450 °C (b).

4. Conclusions

The following conclusions can be drawn from ESR and TSL measurements:

1. The ionizing UV- X- and γ -irradiation of the Bioglass[®] at room temperature leads to generation of stable paramagnetic centers of four types, which have been identified by ESR spectroscopy.

2. Efficiency of generation and type of radiation-induced centers strongly depends on the basic glass composition (*i.e.*, ratio of the network formers to the modifiers) and is independent of the kind of ionizing irradiation and presence of Fr^{3+} impurity.

3. The parameters of the spin Hamiltonian and thermal stability of the radiation-induced centers have been evaluated. It has been found that the RC (1) and RC(4) hole centers can be described in the framework of the models of HC_2 and O^- centers. The RC (2) and RC (3) centers have no analogies in literature and their nature needs additional study.

4. The RC (1) is localized nearest to the ^{23}Na nucleus, because of its superhyperfine structure (L-center), whereas the RC (4) center is not related to the nucleus with magnetic momentum.

5. The RC (3) electron centers cannot be assigned to the thermoluminescence centrum.

6. Pre-treating the samples in the 0.9% NaCl solution and SBF causes the surface coating with composition different from the basic Bioglass[®] composition and influences the process of formation of radiation defects. The process of interaction of physiological solutions with surface artificial material is very complicated and still it is not yet clear in every detail. Studies of the surface coating composition and their influence on the process of formation of radiation-induced volume and surface centers are in progress.

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References

- [1] HENCH L. L., SPLINTER R. J., ALLEN W. C., GREENLEE T. K., *J. Biomed. Mater. Res. Symp.* **2** (1971), 117.
- [2] HENCH L. L., ETHRIDGE E. C., *Biomaterials. An Interfacial Approach*, Acad. Press, New York 1982.
- [3] HENCH L. L., *Materials in Clinical Applications*, [Ed.] P. Vincenzini, Techna 1995, p. 31.
- [4] NAKAMURA T., *ibidem*, p. 35.
- [5] HENCH L. L., *Summary and future directions*. [In] *An Introduction to Bioceramics*, [Eds.] L. L. Hench, J. Wilson, World Sci., Singapore 1993, p. 365.
- [6] KIM C. Y., CLARK A. E., HENCH L. L., *J. Non-Cryst. Sol.* **113** (1989), 195.
- [7] OHTSUKI C., KOKUBO T., TAMAMURO T., *J. Non-Cryst. Sol.* **143** (1992), 84.
- [8] NAKAI Y., *Bull. Chem. Soc. Jpn.* **38** (1965), 1308.
- [9] HASEGAWA A., MIURA M., *Bull. Chem. Soc. Jpn.* **40** (1967), 2553.
- [10] WEEKS R. A., BRAY P. J., *J. Chem. Phys.* **48** (1968), 5.
- [11] GEOFFROY M., TOCHON-DANGUY H. J., *Calcif. Tissue Int.* **34** (1982), S99.
- [12] DOI Y., MORIWAKI Y., AOBA T., KONI M., *ibidem*, p. 547.

- [13] BACQUET G., SBIT M., VIGNOLES M., BONEL G., *Radiat. Effects* **72** (1983), 299.
- [14] SHARROCK P., BONEL G., *Biomaterials* **13** (1992), 755.
- [15] KOKUBO T., *J. Non-Cryst. Sol.* **120** (1990), 138.
- [16] SZARSKA S., SARNOWSKA K., LEWOWSKA L., MAGIERSKI M., *Ceramics* **57** (1998), 211.
- [17] CASTNER T., Jr., NEWELL G.S., HOLTON W.C., *et al.*, *J. Chem. Phys.* **32** (1960), 668.
- [18] GRISCOM D.L., *J. Non-Cryst. Sol.* **40** (1980), 211.
- [19] KLIAVA J., *EPR Spectroscopy of Disordered Solids* (in Russian), Zinatne, Riga 1988.
- [20] BRODBECK C.M., BUKREY R.R., *Phys. Rev. B* **24** (1981), 2334.
- [21] PADLYAK B.V., GUTSZE A., *Appl. Magn. Reson.* **14** (1998), 59.
- [22] PADLYAK B.V., SZARSKA S., *Radiat. Measur.* will be published in 2001.
- [23] SCHREURS J.W.H., *J. Chem. Phys.* **47** (1967), 818.
- [24] ZAMOTRINSKYAY E.A., TORGASHINOVA L.A., ANUFRIENKO V.F., *Neorgan. Materials* **8** (1972), 1138 (in Russian).
- [25] TRUKHIN A.N., *J. Non-Cryst. Sol.* **123** (1990), 250.

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