Current Topics in Biophysics 2010, 33 (suppl A), 163-170

EPR SPECTROSCOPY OF THE RADIATION-INDUCED PARAMAGNETIC CENTERS IN GLASSES

BOHDAN V. PADLYAK[1,2]

[1]Section of Spectroscopy, Institute of Physical Optics, 23 Dragomanov Str., 79-005 Lviv, Ukraine
[2]Division of Spectroscopy of Functional Materials, Institute of Physics, University of Zielona Góra, 4a Szafrana Str., 65-516 Zielona Góra, Poland

Received June 12, 2010; accepted September 4, 2010; published online November 20, 2010.

The X-band EPR spectra of the UV -, *X* -, and γ - irradiated glasses of the SiO_2-Na_2O-CaO-P_2O_5 (Bioglass®) and CaO-Ga_2O_3-GeO_2 systems with different chemical compositions have been investigated at temperatures 77 and 300 K. It was shown that the efficiency of generation of the electron and hole centers in glasses of both systems strongly depends on their basic composition and is almost independent of the type of ionizing radiation and the presence of the non-controlled Fe^{3+} ions and other impurities in the glass network. The spin Hamiltonian parameters and ranges of thermal stability of radiation-induced centers in the investigated glasses are determined and analyzed. The electron structure, features of formation and possible models of the radiation-induced paramagnetic centers in the SiO_2-Na_2O-CaO-P_2O_5 and CaO-Ga_2O_3-GeO_2 glass network have been discussed.

INTRODUCTION

The EPR proves to be a powerful tool for studying of nature and structure of point paramagnetic defects in different materials, including glasses of different compositions. Point paramagnetic defects in crystals and glasses represent impurity transition and rare-earth ions and radiation-induced centers, i.e. electrons and holes, trapped at different sites of crystal lattice and glass network. This article presents the review of our EPR studies of electron and local structure of the radiation-induced paramagnetic centers (PC) in the glasses of SiO_2-Na_2O-CaO-P_2O_5 and CaO-Ga_2O_3-GeO_2 systems.

The alkali silicate phosphate glasses of the SiO_2-Na_2O-CaO-P_2O_5 system are intended to be used in the human body as an implant material, which become attached to living tissue. The glasses, which contain less than about 60 wt.% SiO_2, are called bioactive (Bioglass®). Chemical composition of bioactive glasses is similar to the composition of bones. Bones contain 1/3 organic materials and 2/3 inorganic materials and water. The inorganic part of the bone is composed of the calcium phosphate (crystalline hydroxyapatite (HAP) and non-crystalline calcium orthophosphate), calcium carbonate and small amount of magnesium oxide. Since discovery of the Bioglass® (Hench L.L., Splinter R.J., Allen W.C. & Greenlee T.K., 1971), various kinds of glasses and glass-ceramics (Hench L.L. & Ethridge E.C., 1982; Hench L.L., 1995) as the implant materials for living bones have been found. The Bioglass® surface that can induce the formation of apatite layer *in vivo*, or is pre-coated with apatite layer, demonstrates good bonding with living bones (Kim C.Y., Clark A.E. & Hench L.L., 1989; Ohtsuki C., Kokubo T. & Yamamuro T., 1992; Hench L.L., 1993).

At present time the radiation-induced and impurity paramagnetic point defects are widely studied in phosphate glasses with different compositions. In particular, the EPR spectrum of radiation-induced PO_4^{2-} hole centers in the alkali and alkali-earth phosphate glasses, which is characterized by hyperfine doublet from ^{31}P isotope (nuclear spin $I = 1/2$), were studied by a number of authors (Nakai Y., 1965; Hasegawa A. & Miura M., 1967; Weeks R. A. & Bray P. J., 1967). Different models have been proposed for local symmetry of the PO_4^{2-} radical. In several papers EPR study of radiation-induced defects in hydroxyapatites (Geoffroy M. & Tochon-Danguy H.J., 1982; Doi Y., Moriwaki Y., Aoba T. & Koni M., 1982; Bacquet G., Sbit M., Vignoles M. & Bonel G., 1983; Kokubo T., 1990; Sharrock P. & Bonel G., 1992) were reported. Particularly, in the carbonated HAP F^+ centers (Bacquet G. *et al.*, 1983) were observed. In plasma-sprayed and β - and γ - irradiated HAP the anisotropic EPR signal related to the O^- anion-radicals adjacent to a calcium vacancy was registered (Sharrock P. & Bonel G., 1992). Only in our papers (Padlyak B., Szarska S. & Jungner H., 2000; Padlyak B. & Szarska S., 2004) the nature and structure of four types of radiation-induced PC in the Bioglass® were studied by EPR technique.

The crystals and glasses of the CaO-Ga_2O_3-GeO_2 system, activated with transition and rare-earth ions are

perspective materials for quantum electronics. Three stable crystalline compounds: $Ca_3Ga_2Ge_3O_{12}$ (garnet structure, space group - *Ia3d*), $Ca_3Ga_2Ge_4O_{14}$ (Ca-gallogermanate structure, space group - *P321*) and $Ca_2Ga_2GeO_7$ (gelenite structure, space group – $P\bar{4}2_1m$) exist in the $CaO\text{-}Ga_2O_3\text{-}GeO_2$ ternary system (Damen J.P.M., Pistorius J.A. & Robertson J.M., 1977; Mill B.V., Butashin A.V., Ellern A.M. & Majer A. A., 1981; Mill B.V., Butashin A.V. & Ellern A.M., 1983). Several crystalline compounds were found in the $CaO\text{-}Ga_2O_3$, $CaO\text{-}GeO_2$, and $Ga_2O_3\text{-}GeO_2$ binary systems, particularly the $Ca_3Ga_2O_6$ crystal (Jeevaratnam J. & Glasser F.P., 1961). Glasses of high chemical purity and optical quality with $Ca_3Ga_2Ge_4O_{14}$, $Ca_3Ga_2Ge_3O_{12}$, and $Ca_3Ga_2O_6$ compositions were for the first time obtained by us (Padlyak B.V. & Buchynskii P.P., 1998). Our X-ray diffraction (Padlyak B., Mudry S., Halchak V., Korolyshyn A., Rybicki J. & Witkowska A., 2000) and EXAFS (Extended X-ray Absorption Fine Structure) (Chełstowski D., Witkowska A., Rybicki J., Padlyak B., Trapananti A. & Principi E., 2003) studies of the un-doped glasses with $Ca_3Ga_2Ge_3O_{12}$ and $Ca_3Ga_2Ge_4O_{14}$, and $Ca_3Ga_2O_6$ compositions show that their structures are characterized by short-range chemical ordering similar to the ordering in the corresponding crystals. The EPR spectra of radiation-induced PC in the $Ca_3Ga_2Ge_3O_{12}$ and $Ca_3Ga_2Ge_4O_{14}$ crystals were described earlier in our papers (Nosenko A.E. & Padlyak B.V., 1989; Nosenko A.E., Leshchuk R.Ye., Padlyak B.V. & Sel'skii A.A., 1997). The results of our EPR studies of the radiation-induced centers in glasses of the $CaO\text{-}Ga_2O_3\text{-}GeO_2$ system were already published in (Padlyak B.V., 2003; Padlyak B., Vlokh O. & Jungner H., 2005).

EXPERIMENTAL DETAILS

The first objects of our studies were two types of Bioglass® produced by Jelenia Góra Optical Factory (Poland) with slightly different compositions (in wt.%): 1) 45 SiO_2 : 24.5 Na_2O : 24.5 CaO : 6P_2O_5 (Bioglass® I or BG I, in literature – 45S5 (Hench L.L. *et al.*, 1971)); 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 in the following physiological solutions: 0.9% NaCl and SBF (stimulated body fluid) with pH = 7.4 for 2h. The SBF contains inorganic ions in concentrations close to those in blood plasma (Kokubo T., 1990; Hench L.L., 1995).

The second objects of our studies were glasses of the $CaO\text{-}Ga_2O_3\text{-}GeO_2$ system with the $Ca_3Ga_2Ge_3O_{12}$, $Ca_3Ga_2Ge_4O_{14}$, and $Ca_3Ga_2O_6$ compositions. Chemical composition of obtained glasses was controlled by *X*-ray microanalysis using a "Comeka Comebax" apparatus.

The glass samples for EPR investigations were cut to approximate size of $8\times3\times2mm^3$. The UV-irradiation was carried out at room temperature using a lamp of DKsEL-2000 type (P = 2000 W). The *X* - irradiation was carried out with use of an URS-55A standard apparatus (CuK_α radiation, U = 40 kV, I = 10 mA) at room temperature. Exposition time was equal to 60 min for both types of irradiation. The γ - irradiation of the Bioglass® samples was performed using a ^{90}Sr 40 mCi source (dose 2 Gy). The γ - irradiation of glasses of the $CaO\text{-}Ga_2O_3\text{-}GeO_2$ system was realized in Kyiv Institute of Nuclear Research (Ukraine) with use of a ^{60}Co gun (dose – 1.19×10^4 Gy). Isochronal (20 min) thermal annealing of the irradiated glasses was carried out in air using computer controlled furnace in the 325 ÷ 550 K range. For EPR studies of the glass samples special quartz tubes of high chemical purity were used.

The X-band EPR spectra were registered at temperatures 300 and 77 K using a RADIOPAN SE/X-2544 (Poznań, Poland) and AE-4700 (Lviv, Ukraine) modernized computer controlled commercial spectrometers with cylindrical TM_{110} cavity, operating in the high-frequency (100 kHz) modulation mode of the magnetic field. Microwave frequency in each case was controlled by means of diphenylpicrylhydrazyl (DPPH) *g*-marker ($g = 2.0036 \pm 0.0001$). Parameters of EPR spectra were evaluated using a BRUKER computer simulation program „SimFonia". The number of paramagnetic centers were evaluated using a special spin standard (number of spins $N_S = 5\times10^{15}$ spins/G).

RESULTS AND DISCUSSION

Radiation-induced paramagnetic centers in Bioglass®

It is easy to notice that all investigated Bioglass® samples yields isotropic EPR signals at $g_{eff} = 4.29$ and $g_{eff} = 2.00$. Observed signals are typical for vitreous (or glassy) state (Castner T. Jr., Newell G. S., Holton W. C. & Slichter C. P., 1960; Griscom D.L., 1980; Brodbeck C. M. & Bukrey R. R., 1981; Kliava J., 1988; Padlyak B.V. & Gutsze A., 1998) and were assigned to isolated Fe^{3+} ($3d^5$, $^6S_{5/2}$) ions in octahedral and tetrahedral sites with strong rhombic distortion (Fe^{3+} (I) centers with $g_{eff} = 4.29$) and in octahedral sites with nearly cubic symmetry (Fe^{3+} (II) centers with g_{eff}=2.00). Total amount of Fe^{3+} ions in the BG I samples estimated by EPR is in 5 ÷ 10 times greater than that in the BG II ones and does not exceed 10^{-2} wt.%.

The UV-, *X*-, and γ - irradiation of BG I samples at T = 300 K leads to generation of stable radiation centers (RC) of three types designed as RC (1), RC (2), and RC (3) (Fig. 1). The same irradiation of BG II samples generates, mainly, one stable center, RC (4) (Fig. 2). Detailed EPR spectra analysis shows that the RC (4)

signal were observed also in the BG I samples as a background of the RC (1) signal (Fig. 1) and the RC (2) and RC (3) weak EPR signals were observed also in BG II samples (Fig. 2). Thus, the efficiency of generation of different PC strongly depends on the 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) and in a strong decrease of the amount of RC (1), RC (2), and RC (3) and *vice versa*. As a result the RC (4) signal dominates in BG II samples, whereas the RC (1), RC (2), and RC (3) signals dominate in BG I samples (Figs. 1 and 2). Pre-treatment of the BG I sample in the NaCl solution and SBF leads to a decrease of the amount of RC (2) and an increase of the amount of RC (3), whereas the amount and type of radiation-induced centers in the BG II practically are independent of pre-treatment of samples (Figs. 1 and 2). Types of radiation-induced paramagnetic defects in the BG I and BG II samples are independent of the kind of ionizing radiation (UV, *X*, and *γ*). Also the intensity of EPR signals of the Fe^{3+} (I) and Fe^{3+} (II) impurity centers in the irradiated BG I and BG II samples does not change.

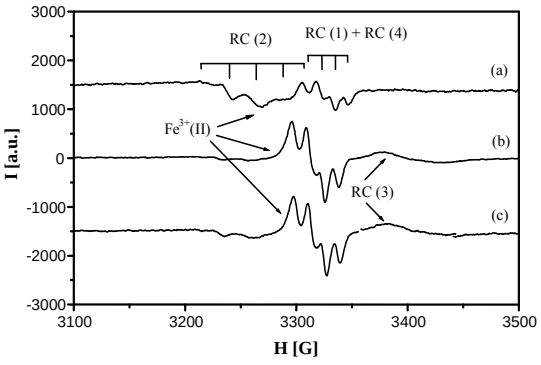

Fig. 1. The X-band EPR spectra of UV-irradiated Bioglass® I, registered at T = 300 K in the as-synthesized (a), pre-treated in the NaCl solution (b) and SBF (c) samples.

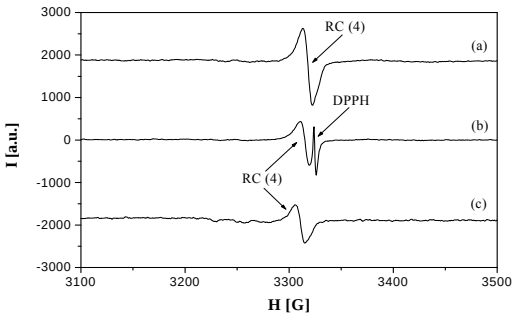

Fig. 2. The X-band EPR spectra of the Bioglass® II, registered at T = 300 K in pre-treated in the SBF and UV-irradiated (a), as-synthesized and *X*-irradiated (b), pre-treated in the NaCl solution and *X*-irradiated (c) samples.

The EPR spectrum of RC (1) is characterized by effective *g*-factor value of the hole type ($g_{\text{eff}} > g_e = 2.0023$) and consists of four equidistant lines of equal intensity (Fig. 1). The RC (1) signal could be explained assuming the hyperfine (HF) interaction of the unpaired electron spin ($S = 1/2$) with the magnetic moment of one of the nearest nucleus with nuclear spin $I = 3/2$. Analysis of the isotopic composition of elements occurring in Bioglass® shows that the source of HF interaction can be a single nucleus of the ^{23}Na isotope ($I = 3/2$, natural abundance – 100%).

The RC (2) EPR spectrum is characterized by practically isotropic hole-like *g*-factor and consists of five approximately equidistant lines with intensities ratio close to 1 : 4 : 6 : 4 : 1, which can be ascribed to the ^{31}P superhyperfine structure (SHF) of stable isotope ($I = 1/2$, natural abundance – 100%). Since the number of components in the SHF structure $N = (2nI + 1) = 5$, it follows that the number of the ^{31}P equivalent nuclei is $n = 4$. Thus, the fivefold SHF splitting of the RC (2) EPR signal is caused by interaction of an unpaired electron spin with four nearest nuclei of the ^{31}P isotope. The EPR spectrum of RC (3) is characterized by a broad ($\Delta H_{pp} \cong 50$G) unresolved signal with *g*-factor of the electron type ($g_{\text{eff}} < g_e = 2.0023$). The EPR spectrum of RC (4) consists of an asymmetric line ($\Delta H_{pp} \cong 9$ G) with a hole-like *g*-factor, which value is the same as for RC (1). All observed EPR spectra of the radiation-induced centers in the BG I and BG II samples are independent of temperature in the 77 ÷ 300 K range.

Presence of the four different types of radiation-induced paramagnetic centers in the Bioglass® network clearly demonstrates isochronal annealing of *X*-irradiated samples (Fig. 3). The intensity of EPR signal related to the RC (1) monotonously decreases with increasing of annealing temperature and completely vanishes at T ≅ 500 K, whereas the intensity of RC (2) EPR signal does not change even after heating up to T > 550 K (Fig. 3, left side). Intensities of EPR signals related to RC (3) and RC (4) monotonously decrease during isochronal annealing (Fig. 3). As a result, the EPR signal related to RC (3) disappears at T ≅ 550 K (Fig. 3, left side), whereas the line related to RC (4) completely disappears at T ≅ 475 K (Fig. 3, right side). The ranges of thermal stability of the radiation-induced centers in Bioglass® are given in Table 1.

Observed EPR spectra of the radiation-induced centers can be described by spin Hamiltonian in the following general form:

$$H = \beta\,\mathbf{H}\cdot g\cdot\mathbf{S} + \mathbf{S}\cdot A\cdot\mathbf{I} + \sum_{i=1}^{4}\mathbf{S}\cdot a_i\cdot\mathbf{I}_i \qquad (1)$$

where β is the Bohr magneton, g is the tensor of electronic Zeeman interaction, A is the tensor of

magnetic hyperfine interaction between the electron of spin $\boldsymbol{S}$ and a nucleus of spin $\boldsymbol{I}$, and a_i is the tensor of magnetic superhyperfine interaction between the electron of spin $\boldsymbol{S}$ and n equivalent nuclei of spin $\boldsymbol{I_i}$. The RC (1) spectrum is described by the first and the second terms, the RC (2) spectrum is described by the first and the third terms, and the RC (3) and RC (4) spectra are described by the first term of the spin Hamiltonian (1). The g, A, and a values for the radiation-induced centers in Bioglass® obtained in the isotropic approximation of the hyperfine and superhyperfine interactions are presented in Table 1.

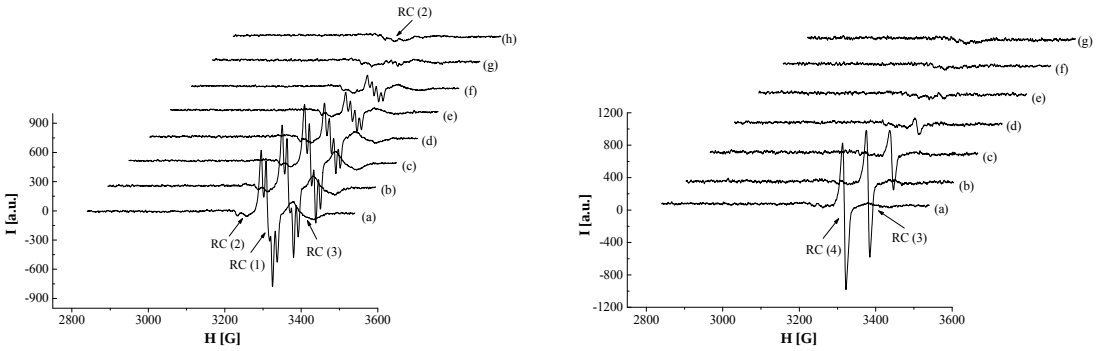

Fig. 3. EPR spectra, registered at T = 300 K in the as-synthesized and *X*-irradiated BG I sample (left side) and pre-treated in NaCl solution and *X*-irradiated BG II sample (right side) after isochronal annealing (20 min) in the air at the following temperatures: 325 K (a), 375 K (b), 400 K (c), 425 K (d), 450 K (e), 475 K (f), 500 K (g), and 550 K (h).

Table 1. The spin Hamiltonian parameters obtained as the best fit of the experimental (T = 300 K) and simulated EPR spectra and ranges of thermal stability of the radiation-induced centers in the Bioglass®

Centers number	Thermal stability	*g*-tensor values		*A*-tensor values		*a*-tensor values	
		$g_{\|\|}$	$g_{\perp}$	$A_{\|\|}$, G	$A_{\perp}$, G	$a_{\|\|}$, G	$a_{\perp}$, G
RC (1)	≤ 475 K	2.009±0.001	2.005±0.001	12±1	12±1	–	–
RC (2)	> 500 K	2.048±0.001	2.048±0.001	–	–	23±2	23±2
RC (3)	≤ 500 K	1.965±0.005	1.953±0.005	–	–	–	–
RC (4)	≤ 425 K	2.009±0.001	2.005±0.001	–	–	–	–

The observed hole centers in the glasses can be assigned to an ensemble of O^- centers, i.e., holes, trapped at non-bridging oxygen with different local environment. On the basis of presented EPR and referenced data we can conclude that the RC (1) and RC (4) can be described in the framework of models of the HC_2 (Schreurs J.W.H., 1967) and O^- (Zamotrinskaya E.A., Torgashinova L.A. & Anufrienko V.F., 1972) centers proposed for alkali silicate glasses with high amount of the alkali modifiers. In accordance to these models the RC (4) is a hole, captured on a Si-O tetrahedron, which contains 3 non-bridging oxygens and the wave function of hole is presumable largely restricted to the 3 non-bridging oxygens (Schreurs J.W.H., 1967). The RC (1) is the O^- center, localized nearest to the Na^+ ion. It is the so-called L-center, ($Si - O^- - Na^+$) (Trukhin A.N., 1990), which is characterized by four-component hyperfine structure in their EPR spectrum, caused by one nucleus of the ^{23}Na isotope. One can notice that both RC (1) and RC (4) are characterized by high, but slightly different thermal stability (Table 1).

The RC (2) center can be interpreted as an electron, trapped at oxygen vacancy. The SHF structure of the RC (2) centers could be explained by the interaction of an unpaired electron spin with four nearest ^{31}P nuclei of the glass network. The RC (2) centers in the Bioglass® network are characterized by very high thermal stability and have no analogies in literature. The electron RC (3) centers are characterized by inhomogeneously broadened EPR line ($\Delta H_{pp} \cong 50$ G) and cannot be assigned to the well-known E′(Si) centers (Griscom D. L., 1976; Griscom D. L., 1979). Inhomogeneous broadening of the RC (3) EPR signal can be connected with the presence of several volume and surface centers of the electron type with different local environment,

which give statistically-distributed *g*-factor values that form the observed EPR lineshape. Nature of the RC (3) needs additional study by magnetic resonance and other spectroscopic methods.

Radiation-induced paramagnetic centers in glasses of the CaO-Ga_2O_3-GeO_2 system

The UV-irradiation of Ge-containing glasses with $Ca_3Ga_2Ge_3O_{12}$ and $Ca_3Ga_2Ge_4O_{14}$ compositions induces stable PC designed as type I (Fig. 4, spectra a, b), whereas in the $Ca_3Ga_2O_6$ glasses only PC of type II (Fig. 4, spectrum c) were detected. The *X*-irradiation of Ge-containing glasses leads to generation of stable PC of both types (Fig. 5, a, b), whereas in the $Ca_3Ga_2O_6$ glasses only stable PC of type II (Fig. 5, c) were induced. In the γ - irradiated CaO-Ga_2O_3-GeO_2 glasses similar EPR spectra as in the *X*-irradiated glasses were observed. The number of both types of centers depends on glass composition and the generation efficiency decreases for centers of type I and increases for centers of type II with decreasing of the GeO_2 content in the glass composition (Figs. 4 and 5). Observed peculiarities of the PC formation are characteristic also for irradiated glasses of the CaO-Ga_2O_3-GeO_2 system, doped with transition and rare-earth metals ions.

The radiation-induced PC can be related to non-controlled impurities or intrinsic defects of the glass network. Glasses of the CaO-Ga_2O_3-GeO_2 system are characterized by high chemical purity (Padlyak B.V. & Buchynskii P.P., 1998), but in all doped and un-doped glasses the Fe^{3+} ($3d^5$, $^6S_{5/2}$) impurity ions are presented (Padlyak B.V. & Gutsze A., 1998; Padlyak B. *et al.*, 2000). Total amount of the Fe^{3+} ions in the best samples doesn't exceed 10^{-3} wt.%. Intensity of EPR spectra of the Fe^{3+} and other (Cr^{3+}, Mn^{2+}, *etc.*) paramagnetic ions in the doped CaO-Ga_2O_3-GeO_2 glasses was not changed after UV-, *X*-, and γ-irradiation. Therefore, the formation mechanism of radiation-induced PC in glasses of the CaO-Ga_2O_3-GeO_2 system is related to the intrinsic defects of the glass network.

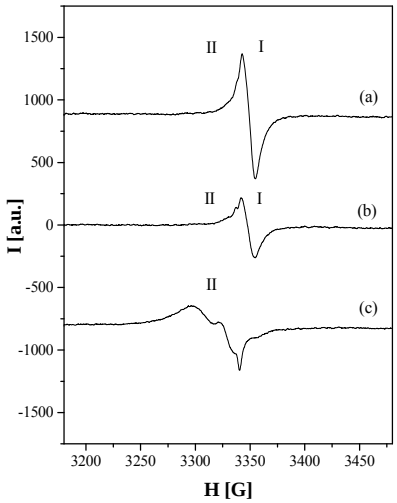

Fig. 4. The X-band EPR spectra of the UV-irradiated glasses with $Ca_3Ga_2Ge_4O_{14}$ (a), $Ca_3Ga_2Ge_3O_{12}$ (b), and $Ca_3Ga_2O_6$ (c) compositions, registered at T = 300 K.

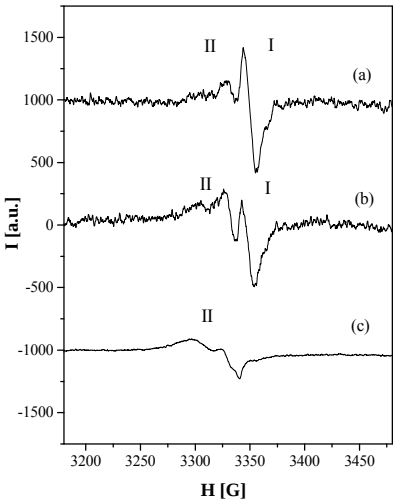

Fig. 5. The X-band EPR spectra of the *X*-irradiated glasses with $Ca_3Ga_2Ge_4O_{14}$ (a), $Ca_3Ga_2Ge_3O_{12}$ (b) and $Ca_3Ga_2O_6$ (c) compositions, registered at T = 300 K.

Analysis of the EPR spectra, presented in Figs. 4 and 5, show that these spectra belong to centers of two different types. „Pure" EPR spectrum of PC of type I is observed in the UV-irradiated $Ca_3Ga_2Ge_4O_{14}$ glasses (Fig. 4, spectrum a), whereas „pure" EPR spectrum of PC of type II is observed in the UV-, *X*-, and γ-irradiated $Ca_3Ga_2O_6$ glasses (Figs. 4 and 5, spectrum c). These „pure" EPR spectra were used for analysis and evaluation of the *g*-factor values for PC of two types. No better resolution of the complex EPR lines in all investigated glasses was observed at T = 77 K. The inhomogeneous broadening of EPR lines for both types of PC is related to statistical distribution of their local axes and *g*-factor values. Using the experimental *g* values, peak-to-peak linewidth, and the lineshape, it was possible to simulate the EPR spectra. Best fitting to the experimental spectra was obtained for *g*-factors, which are given in Table 2. For comparison Table 2 contains also the *g*-factors for radiation-induced PC in the GeO_2 glass, $Ca_3Ga_2Ge_4O_{14}$ disordered and $Ca_3Ga_2Ge_3O_{12}$ ordered crystals. The EPR spectrum of centers of type I was described by a spin Hamiltonian of axial symmetry with *g*-tensor values, which are characteristic for centers of the electron type ($g_1 < g_e = 2.0023$). The EPR

spectrum of centers of type II was described by a spin Hamiltonian of rhombic symmetry with *g*-tensor values, which are characteristic for centers of the hole type ($g_{II} > g_e = 2.0023$).

The observed electron PC of type I can be identified as Ge-related centers, because these centers are induced in the Ge-contained glasses, exclusively. Similar centers were observed earlier in the GeO_2 glasses and crystals (Pursell T.A. & Weeks R.A., 1969), Ge-doped silica fiber (Friebele E.J., Griscom D.L., & Sigel G.H., Jr., 1974) and other germanate glasses (Margaryan A. & Pilavin M.A., 1993). According to referenced data, presented in Table 2, the Ge-related PC in the glass network are characterized by axially symmetric *g*-factor and are assigned to E′(Ge) centers, i.e. electrons, trapped at the sites of oxygen vacancies in the dangling sp^3 hybrid orbital of Ge. Geometry and theoretical *g*-tensor values for E′(Ge) center in the glass network are given in (Friebele E.J. *et al.*, 1974). The E′(Ge) centers are analogous to well-known silicon E′(Si) centers (Griscom D. L., 1976; Griscom D. L., 1979).

Table 2. The *g*-tensor principal values for hole and electron radiation-induced centers in the GeO_2 glass and crystals and glasses of the $CaO\text{-}Ga_2O_3\text{-}GeO_2$ system

Glasses and crystals	Type of centers	*g* - tensor values			Refs.
		g_{xx}	g_{yy}	g_{zz}	
GeO_2 (glass)	E′ (Ge)	1.9944±0.0008	1.9944±0.0008	2.0010±0.0008	(Pursell T.A. *et al.*, 1969)
$CaO\text{-}Ga_2O_3\text{-}GeO_2$ (glass)	E′(Ge)*	1.996±0.002	1.996±0.002	2.001±0.002	(Padlyak B.V., 2003)
$Ca_3Ga_2Ge_3O_{12}$ (crystal)	$Ge^{3+}_{(d)}$ #	2.008±0.001	2.008±0.001	2.008±0.001	(Nosenko A.E. *et al.*, 1989)
$CaO\text{-}Ga_2O_3\text{-}GeO_2$ (glass)	O^{-*}	2.017±0.002	2.009±0.002	2.0033±0.0001	(Padlyak B.V., 2003)
$Ca_3Ga_2Ge_4O_{14}$ (crystal)	O^- (1)	2.0180±0.001	2.0180±0.001	2.0180±0.001	(Nosenko A.E. *et al.*, 1997)
	O^- (1)	2.0180±0.001	2.0180±0.001	2.0180±0.001	

Note: *The ensembles of E′(Ge) and O^- centers were observed in glasses of the $CaO\text{-}Ga_2O_3\text{-}GeO_2$ system;
#Superhyperfine interaction ($a \cong 6$ G) with 2 nuclei of the ^{69}Ga and ^{71}Ga isotopes ($I = 3/2$) was observed.

The EPR spectrum of the E′(Ge) centers in $CaO\text{-}Ga_2O_3\text{-}GeO_2$ glasses are characterized by the largest linewidth in comparison with analogous centers in the GeO_2 glasses and crystals (Pursell T.A. & Weeks R.A., 1969; Margaryan A. & Pilavin M.A., 1993) and Ge-doped silica fiber (Friebele E.J. *et al.*, 1974). That can be connected with the presence of several types of E′(Ge) centers with different local environment, which give slightly shifted and statistically distributed *g*-factor values and form the observed EPR lineshape. Presence of several types of the E′(Ge) centers in the $CaO\text{-}Ga_2O_3\text{-}GeO_2$ glass network clearly demonstrate isochronal annealing of the irradiated samples (Fig. 6). With increasing annealing temperature a better resolution of the E′(Ge) EPR spectra was observed (Fig. 6, left side).

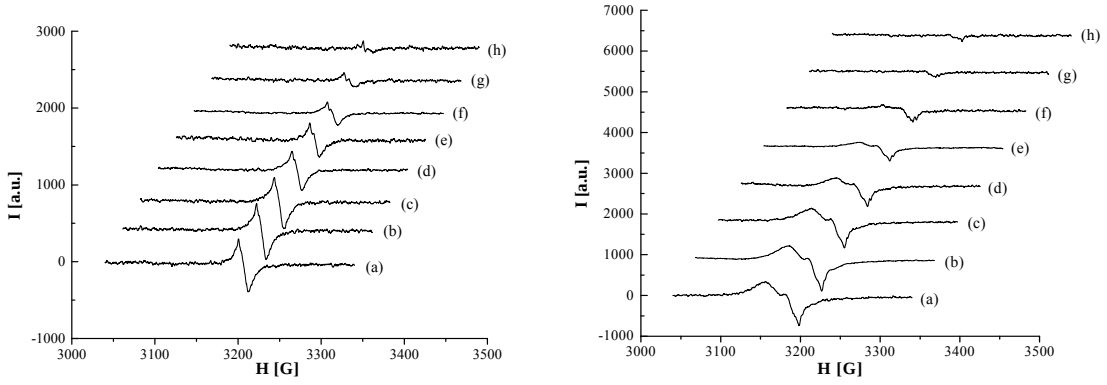

Fig. 6. EPR spectra of the E′(Ge) (left side) and O^- (right side) centers, registered at T = 300 K in the UV-irradiated glasses with $Ca_3Ga_2Ge_3O_{12}$ and $Ca_3Ga_2O_6$ (c) compositions, respectively after isochronal annealing (20 min) in the air at following temperatures: 325 K (a), 375 K (b), 400 K (c), 425 K (d), 450 K (e), 475 K (f), 500 K (g) and 550 K (h).

The EPR spectrum of *X*- and γ - induced hole centers of type II in the Ge-contained glasses (Fig. 5, spectra a-c) is similar to the spectrum of UV-induced hole centers in the $Ca_3Ga_2O_6$ non-germanate glasses (Fig. 4,

spectrum c). It is characterized by inhomogeneously broadened linewidth, caused by statistical distribution of the *g* - tensor values. Similar EPR spectra were observed in a number of irradiated silicate glasses with different composition and were assigned to the HC_1 hole centers (Schreurs J.W.H., 1967; Zamotrinskaya E.A. *et al.*, 1972; Griscom D.L., 1976). The *g*-factor values of hole centers in the $CaO\text{-}Ga_2O_3\text{-}GeO_2$ glasses are closely similar to *g* values of the HC_1 centers in silicate glasses and O^- centers in the $Ca_3Ga_2Ge_4O_{14}$ disordered crystals (Table 2). Because the local structure and chemical composition of the $CaO\text{-}Ga_2O_3\text{-}GeO_2$ glasses and $Ca_3Ga_2Ge_4O_{14}$ disordered crystals are closely similar (Padlyak B. *et al.*, 2000; Chełstowski D. *et al.*, 2003) the observed hole centers in the glasses can be assigned to an ensemble of O^- centers, i.e., holes, trapped at non-bridging oxygen with different local environment. Better resolution in EPR spectra of the O^- centers was not observed with the increase in temperature of isochronal annealing (Fig. 6, right side). This result shows that different O^- centers in the $CaO\text{-}Ga_2O_3\text{-}GeO_2$ glass network are characterized by the same thermal stability.

CONCLUSIONS

Based on the presented results it was concluded that:

1) The ionizing UV -, *X* -, and γ - irradiation of the bioactive glass (Bioglass®) at room temperature leads to generation of four types stable paramagnetic centers that have been identified by EPR spectroscopy.

2) The efficiency of generation and type of radiation-induced paramagnetic centers strongly depends on the basic bioactive glass composition (i.e., ratio of the network former to the modifiers) and is independent of the kind of ionizing radiation and presence of the Fe^{3+} non-controlled and other paramagnetic impurity ions.

3) The spin Hamiltonian parameters and ranges of thermal stability for all radiation-induced centers in Bioglass® have been evaluated. The RC (1) and RC (4) hole centers can be described in the framework of models of the HC_2 and O^- hole centers, respectively. The RC (1) is localized nearest to the ^{23}Na nucleus (L-center), whereas the RC (4) center is not related to the nucleus with magnetic moment. The RC (2) can be interpreted as an electron trapped at oxygen vacancy. The nature of the RC (3) electron center needs additional study by different spectroscopic methods.

4) The EPR spectroscopy data show good correlation with thermally-stimulated luminescence (TSL) results. Particularly, the TSL glow curves, peaked at 370-380 K, 420-430 K, and 690-710 K (Padlyak B. *et al.*, 2000) were assigned to the RC (4), RC (1), and RC (2), respectively.

5) Pre-treatment of the Bioglass® samples in the 0.9% NaCl solution and SBF cause the surface coating with composition different from the basic Bioglass® composition and influences on the process of radiation-induced defects formation. Process of interaction of the physiological solution with surface artificial material is very complicated and at the present time it is not yet clear in every detail.

6) The formation mechanism of radiation-induced defects in the $CaO\text{-}Ga_2O_3\text{-}GeO_2$ glasses depends on the glass composition and kind of ionizing radiation. Particularly, the electron excess E′(Ge) and hole trapped O^- centers stable at room temperature coexist in the *X*- and γ - irradiated $Ca_3Ga_2Ge_4O_{14}$ and $Ca_3Ga_2Ge_3O_{12}$ glasses, whereas in the $Ca_3Ga_2O_6$ glasses the UV-, *X*-, and γ- irradiation induce stable O^- centers, only.

7) Structural disordering leads to a better stabilization of the radiation-induced defects in solids, because the thermal stability of the radiation-induced PC in ordered $Ca_3Ga_2Ge_3O_{12}$ and compositionally (or substitutionally) disordered $Ca_3Ga_2Ge_4O_{14}$ crystals is lower in comparison with glasses of the same chemical composition. In disordered $Ca_3Ga_2Ge_4O_{14}$ crystals the UV- and *X*-radiation generate the O^- hole centers, stable at room temperature and in the $Ca_3Ga_2Ge_3O_{12}$ ordered crystals *X* - and γ - radiation induce the $Ge^{3+}_{(d)}$ centers, stable at liquid nitrogen temperatures, exclusively.

8) In the $Ca_3Ga_2Ge_4O_{14}$ disordered crystals two types of radiation-induced O^- centers with different *g*-values and axes orientations were observed, whereas structural disordering of the $CaO\text{-}Ga_2O_3\text{-}GeO_2$ glasses allows obtaining an ensemble of the O^- centers with statistically distributed *g*-tensor principal values.

9) The TSL glow curves show good correlation with EPR spectra of the same irradiated glasses of the $CaO\text{-}Ga_2O_3\text{-}GeO_2$ system. Particularly, the TSL band, peaked at 230°C in γ - and *X* - irradiated Ge-contained glasses as well as in the γ -, *X* - irradiated glass with $Ca_3Ga_2O_6$ composition is assigned to recombination of the O^- centers. The TSL band, peaked at 280°C in the γ- and *X* - irradiated Ge-contained glasses is attributed to recombination of the E′(Ge) centers.

REFERENCES

Bacquet G., Sbit M., Vignoles M. & Bonel G. (1983). F+ centre in (CaSO4) carbonated hydroxyapatite. *Radiat. Effects*, **72**, 299-302.

Brodbeck C. M. & Bukrey R. R. (1981). Model calculations for the coordination of Fe^{3+} and Mn^{2+} ions in oxide glasses. *Phys. Rev. B.* **24**, No. 5, 2334-2342.

Castner T. Jr., Newell G. S., Holton W. C. & Slichter C. P. (1960). Note on the paramagnetic resonance of iron in glass. *J. Chem. Phys.* **32**, 668-673.

Chełstowski D., Witkowska A., Rybicki J., Padlyak B., Trapananti A. & Principi E. (2003). EXAFS study of glasses of the $CaO\text{-}Ga_2O_3\text{-}GeO_2$ system *Opt. Appl.* **XXXIII**, 125-132.

Damen J.P.M., Pistorius J.A. & Robertson J.M. (1977). Calcium-gallium-germanium garnet as a substrate for magnetic bubble applications. *Mater. Res. Bull.* **12**, 73-75.

Doi Y., Moriwaki Y., Aoba T. & Koni M. (1982). ESR on the hydroxyl ion vacancies in the apatites. *Calcif. Tissue Int.* **34**, 547-551.

Friebele E.J., Griscom D.L., & Sigel G.H., Jr. (1974). Defect centers in a germanium-doped silica-core optical fiber. *J. Appl. Phys.* **45**, No. 8, 3424-3428.

Geoffroy M. & Tochon-Danguy H.J. (1982). ESR identification of radiation damage in synthetic apatites: a study of the carbon-13 hyperfine coupling. *Calcif. Tissue Int.* **34**, S99-S102.

Griscom D.L. (1976) Defects and their structure in nonmetallic solids. Eds. Henderson B. & Hugs A.E. Plenum Press, New York.

Griscom D.L. (1979). E' center in glassy SiO_2: microwave saturation properties and confirmation of the primary ^{29}Si hyperfine structure. *Phys. Rev. B*, **20**, No. 5, 1823-1834.

Griscom D.L. (1980). Defects in glasses. *J. Non-Cryst. Sol.* **40,** 211-269.

Hasegawa A. & Miura M. (1967). The electron spin resonance of γ-irradiated sodium phosphate glasses. *Bull. Chem. Soc. Jpn.* **40**, 2553-2558.

Hench L.L., Splinter R.J., Allen W.C. & Greenlee T.K. (1971). Bonding mechanisms at the interface of ceramic prosthetic materials. *J. Biomed. Mater. Res. Symp.* **2**, 117-141.

Hench L.L. & Ethridge E.C. (1982). Biomaterials, an interfacial approach. Academic Press, New York.

Hench L.L. (1993). Summary and future directions. In: An introduction to bioceramics. Eds. Hench L.L. & Wilson J. World Scientific, Singapore.

Hench L.L. (1995). Materials in clinical applications. Ed. Vincenzini P. Techna.

Jeevaratnam J. & Glasser F.P. (1961). The system CaO – Ga_2O_3. *J. Amer. Ceram. Soc.* **44**, No. 11, 563-566.

Mill B.V., Butashin A.V. & Ellern A.M. (1983). Germanates with $Ca_3Ga_2Ge_4O_{14}$ structure. *Izv. Akad. Nauk SSSR, Ser. Neorgan. Mater.* **19**, 1715-1717 (in Russian).

Kim C.Y., Clark A.E. & Hench L.L. (1989). Early stages of calcium-phosphate layer formation in bioglasses. *J. Non-Cryst. Sol.* **113,** 195-202.

Kliava J. (1988). EPR spektroskopia neuporiadochennych tverdych tel (EPR spectroscopy of disordered solids), Zinatne, Riga, (in Russian).

Kokubo T. (1990). How useful is SBF in predicting *in vivo* bone bioactivity? *J. Non-Cryst. Sol.* **120**, 138-138.

Margaryan A. & Pilavin M.A. (1993) Germanate glasses: structure, spectroscopy, and properties. Artech House, Boston – London.

Mill B. V., Butashin A.V., Ellern A.M. & Majer A. A. (1981). Phases formation in CaO-Ga_2O_3-GeO_2 system. *Izv. Akad. Nauk SSSR, Ser. Neorgan. Mater.* **17**, No. 9, 1648-1653 (in Russian).

Nakai Y. (1965). Electron paramagnetic resonance study of γ-ray irradiated phosphate glasses *Bull. Chem. Soc. Jpn.* **38**, 1308-1314.

Nosenko A.E. & Padlyak B.V. (1989). Low-temperature radiation-generated paramagnetic centers in $Ca_3Ga_2Ge_3O_{12}$ crystals. *Sov. Phys. Solid State* **31**, No. 2, 317-319.

Nosenko A.E., Leshchuk R.Ye., Padlyak B.V. & Sel'skii A.A. (1997). Radiation-induced paramagnetic centers in $Ca_3Ga_2Ge_4O_{14}$ crystals *Phys. Solid State* **39**, No. 6, 938-942.

Ohtsuki C., Kokubo T. & Yamamuro T. (1992). Mechanism of apatite formation on CaO-SiO_2-P_2O_5 glasses in a simulated body fluid. *J. Non-Cryst. Sol.* **143**, 84-92.

Padlyak B.V. & Gutsze A. (1998). EPR study of the impurity paramagnetic centers in (CaO-Ga_2O_3-GeO_2) glasses. *Appl. Magn. Reson.* **14**, 59-68.

Padlyak B.V. & Buchynskii P.P. (1998) IR-transparent optical glass. *Patent of Ukraine*, No. **UA 25235 A** (in Ukrainian).

Padlyak B., Szarska S. & Jungner H. (2000). Radiation-induced paramagnetic centers in bioglass®. *Opt. Appl.* **XXX**, 709-717.

Padlyak B., Mudry S., Halchak V., Korolyshyn A., Rybicki J. & Witkowska A. (2000). The structure of CaO-Ga_2O_3-GeO_2 glasses: *X*-ray and molecular dynamics simulation studies *Opt. Appl.* **XXX**, 691-699.

Padlyak B.V. (2003). Radiation-induced centers in glasses of the CaO-Ga_2O_3-GeO_2 system. *Radiation Effects & Defects in Solids*, **158**, Nos. 1-6, 411-418.

Padlyak B. & Szarska S. (2004). EPR spectroscopy of irradiated bioactive glasses. *Funct. Mater.* **11**, 116-121.

Padlyak B., Vlokh O. & Jungner H. (2005). Thermally-stimulated luminescence of radiation-induced defects in the glasses of CaO-Ga_2O_3-GeO_2 system. *Ukr. J. Phys. Opt.* **6**, No. 2, 55-62.

Pursell T.A. & Weeks R.A. (1969). Radiation-induced paramagnetic states of some intrinsic defects in GeO_2 glasses and crystals. *J. Phys. Chem. Glasses* **10**, 198-208.

Schreurs J.W.H. (1967). Study of some trapped hole centers in *X* - irradiated alkali silicate glasses. *J. Chem. Phys.* **47**, 818-830.

Sharrock P. & Bonel G. (1992). Color centers in plasma-sprayed hydroxylapatite *Biomaterials*, **13**, 755-757.

Trukhin A.N. (1990). Localized states of silicon dioxide, sodium and lead silicate glasses *J. Non-Cryst. Sol.* **123**, 250-257.

Weeks R. A. & Bray P. J. (1967). Electron spin resonance spectra of gamma-ray-irradiated phosphate glasses and compounds. Oxygen vacancies. *J. Chem. Phys.* **48**, 5-13.

Zamotrinskaya E.A., Torgashinova L.A. & Anufrienko V.F. (1972). On the nature of "hole" centers in the irradiated alkali silicate glasses. *Izv. Akad. Nauk SSSR, Ser. Neorgan. Mater.* **8**, No. 6, 1136-1140 (in Russian).