EPR STUDIES OF RADIATION-INDUCED CENTERS IN CRYSTALLINE BARIUM DITHIONATE DIHYDRATE

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The properties of barium dithionate powder specimens subjected to gamma and ultraviolet (UV) irradiation have been studied by electron paramagnetic resonance (EPR) spectroscopy. It has been found that gamma irradiation gives rise to the formation of radicals of at least five types, the EPR spectra of which are characterized by different parameters. For two of them, the A-tensors have been determined; namely, $A_{zz} \approx A_{yy} = 11.65$ mT and $A_{xx} = 16.64$ mT for R_1 (SO_3^-) radical, and $A_{zz} \approx A_{yy} = 10.3$ mT and $A_{xx} = 14.73$ mT for R_2 one. Short-wave UV irradiation of identical specimens has been demonstrated to create paramagnetic centers of several types, including SO_3^- radicals. The EPR parameters of those centers have been determined.

1. Introduction

Crystalline barium dithionate dihydrate ($BaS_2O_6 \times \times 2H_2O$) is a promising material for manufacturing the dosimetric EPR sensors of gamma and beta radiation [1–4]. For the purposes of EPR dosimetry, barium dithionate powder specimens are used, because, provided the definite conditions of recording EPR spectra, a single narrow line of SO_3^- radicals, the intensity of which is proportional to the exposure dose, is observed in the irradiated powders concerned. In work [5], the results of EPR studies dealing with the accumulation of SO_3^- radicals in gamma-irradiated powder specimens were reported, and the values of some parameters of their EPR spectra were presented; in particular, $g_{\text{powder}} = 2.0036$, the EPR line halfwidth $\Delta H_{\text{powder}} = 0.55$ mT, and the isotropic constant of superfine interaction with the nuclear spin of the sulfur isotope ^{33}S $A_{\text{powder}} \approx 11.5$ mT. SO_3^- radicals in natural $BaSO_4$ single crystals were also studied [6]; those crystals have the same orthorhombic symmetry as $BaS_2O_6 \cdot 2H_2O$ crystals do [7]. The authors of work [6] showed that there are several types of paramagnetic centers in this material, and some of them can occupy two magnetically nonequivalent states. Their spectra are described by different EPR parameters. Therefore, it was reasonable to expect that radicals of several types could be formed in barium dithionate as well. Really, the authors of work [8], while simulating the experimental spectrum, have demonstrated that it is a complex one and can be described as that composed of four lines with different halfwidths and anisotropic g-factors.

This work aimed at studying, by the method of EPR spectroscopy, the radiation-induced centers in powder specimens of crystalline barium dithionate dihydrate, which emerge under the influence of gamma and UV irradiation, as well as due to the annealing of initial and irradiated specimens, and form the spectrum that is used in EPR dosimetry.

2. Experimental Technique and Materials

EPR measurements were carried out on a Varian E-12 radiospectrometer in the 3-cm range (the X-range); the frequency of magnetic field modulation was 100 kHz, the measurements were carried on at room temperature ($20 \div 25$ °C). The signal of Cr^{3+} ions in MgO ($g = 1.980$) [9] was used as a reference one for the determination of the g-factor values and the relative intensities of barium dithionate EPR lines.

Specimens were irradiated with either gamma rays emitted by a ^{60}Co source or UV rays radiated by a PRK-4 medium pressure mercury tube. Irradiation of the specimens was carried on at room temperature and in atmospheric environment.

Powder specimens were composed of a fine-crystalline synthesized substance. There was no additional treatment of powders before specimen fabrication.

3. Experimental Results and Their Discussion

The EPR spectrum of irradiated barium dithionate powder specimens consists of several lines which correspond to various paramagnetic centers (radicals). Therefore, one may expect that the relaxation times of those centers are different; this hypothesis can be verified in an experiment on the saturation of the EPR spectrum. Really, the shape and the amplitude of the central sections of the EPR spectra (leaving the lines of superfine structure aside) obtained for an exposure dose

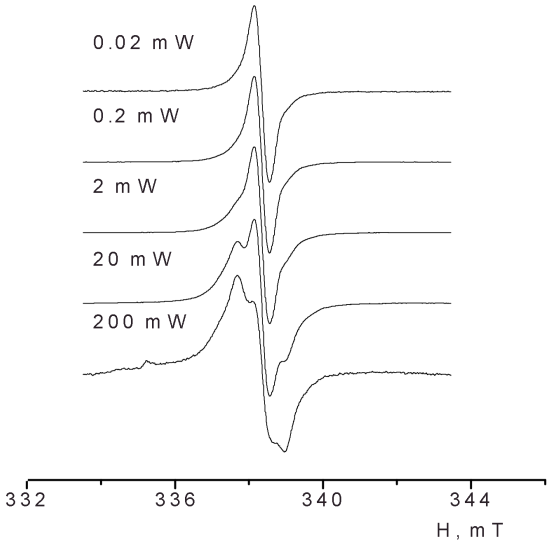

Fig. 1. Shapes of the central part of the EPR spectrum of gamma irradiated barium dithionate powder specimens for various UHF powers (indicated near the corresponding curve)

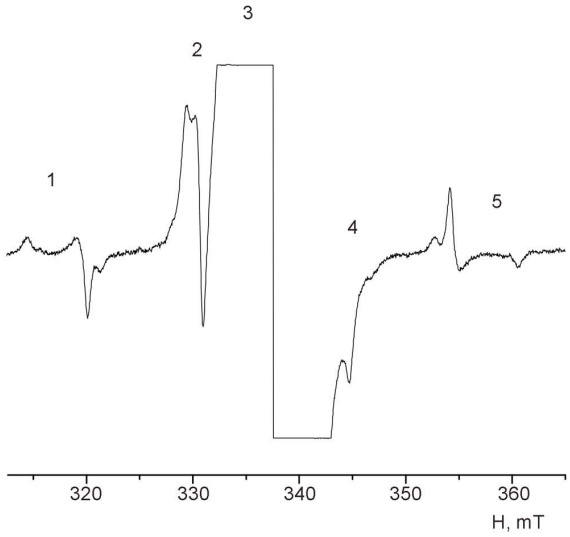

Fig. 2. EPR spectrum of a gamma irradiated barium dithionate powder specimen at a high amplification factor and in a wide range of the magnetic field scanning. Groups of lines *1, 2, 4*, and *5* stem from the superfine interaction with the sulfur isotope ^{33}S, and line 3 is associated with sulfur isotopes with zero nuclear spins

of about 10 kGy depend on the ultrahigh frequency (UHF) power (Fig. 1). The EPR spectra recorded for specimens irradiated at low-exposure doses of about 80 Gy, but at considerable UHF powers (20–200 mW), can be approximated by only four EPR lines with different halfwidths and different g-tensors. The fitting parameters of the experimental spectrum approximation (more precisely, its central section) are listed in Table 1. At exposure doses of 10^1–10^4 Gy and a low power of the EPR signal of about 2 mW, the total halfwidth of the complicated EPR line $H_{pp} = (0.42 \pm 0.02)$ mT and its g-factor $g_{\text{powder}} = 2.0026 \pm 0.0005$. In general, the line halfwidth depends on the exposure dose, and the data obtained for two exposure doses confirm this conclusion, although the detailed researches have not been carried out yet. If the UHF power is low (of about 2 mW), $H_{pp} = 0.28$ mT at an exposure dose of 80 Gy, and $H_{pp} = 0.52$ mT at 50 kGy. The values of g-factors and line halfwidths, which are quoted in Table 1, differ from those reported in work [8].

In the EPR spectrum (Fig. 2) recorded in a wide range of the applied magnetic field of about 50 mT and in the regime with high EPR signal amplification (the amplification factor was 1000 times higher), one can distinguish 5 groups of lines. Line groups *1, 2, 4*, and *5* originate from the superfine interaction between the electron spin of SO_3^- radical ($S = 1/2$) and the nuclear spin of the sulfur isotope ^{33}S (natural abundance of 0.76% and $I = 3/2$). Line 3 (with the cut-off amplitude) is associated with the rest of sulfur isotopes (natural abundance of 99.24% and $I = 0$). The contribution given by the ^{33}S isotope can be interpreted as that due to the presence of radicals of two types with different parameters. For convenience, we denote radicals that are responsible for superfine spectra as R_1 ($R_1 \approx SO_3^-$) and R_2 (the centers of this type has not been identified, but such radicals may prove to be SO_3^- as well and be located on the surface of microcrystals). The superfine interaction constants, which describe the EPR spectrum of R_1 radical, are $A_{zz} \approx A_{yy} = 11.5$ mT and $A_{xx} = 15.64$ mT; for the spectrum of R_2 radical, these are $A_{zz} \approx A_{yy} = 10.73$ mT and $A_{xx} = 14.73$ mT.

The isothermal (at various temperatures of 55, 60, 70, 85, 100, and 130 °C) annealing of powder specimens, which were preliminarily gamma-irradiated at various exposure doses of 1, 10, 10^2, 10^3, 10^4, and 5×10^4 Gy, revealed that radicals of several types are formed in the

T a b l e 1. Parameters used for simulating the central section of the EPR spectrum of a gamma-irradiated barium dithionate powder specimen (the UHF power is 5 mW)

Spectrum	Line shape	$g_\parallel$	$g_\perp$	ΔH_{pp}, mT
R_1, axial	Lorentzian	1.9998	2.0010	0.51
R_2, axial	Gaussian	2.0045	2.0063	0.51
R_3, axial	Gaussian	2.0025	2.0032	0.336
R_4, axial	Gaussian	2.0025	2.0086	0.37

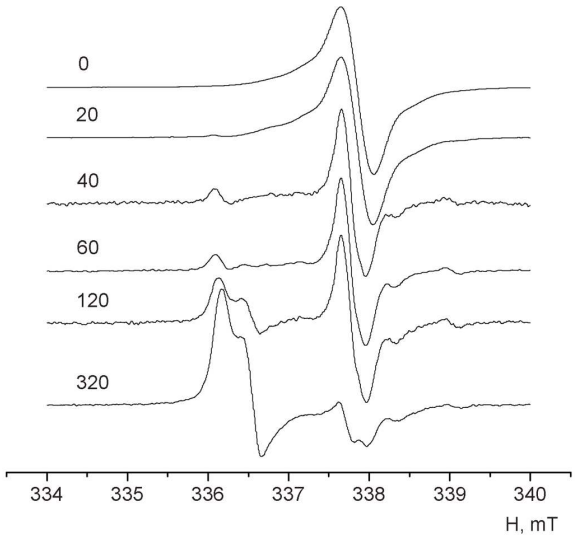

Fig. 3. EPR spectra of barium dithionate powder specimens gamma-irradiated at a dose of 5×10^4 Gy for various times of annealing at a temperature of 130 °C (indicated near the corresponding curve in minute units)

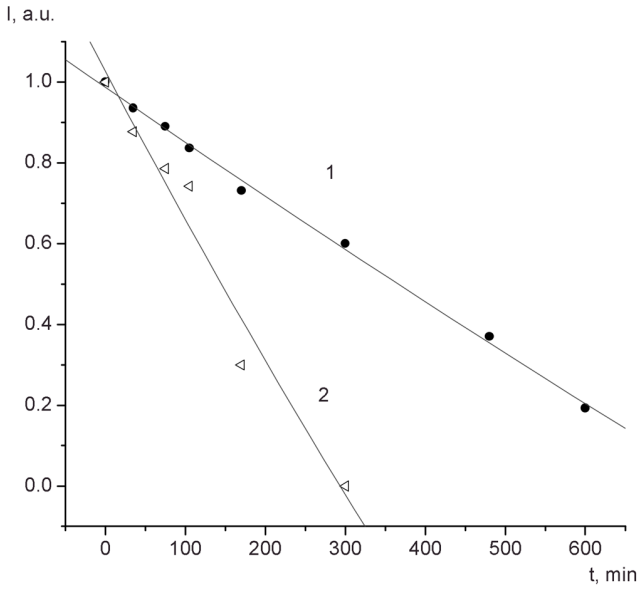

Fig. 4. Dependences of the EPR signal intensity (the concentration of radicals) on the time of the annealing at 85 °C for various exposure doses: 10 (*1*) and 10^4 Gy (*2*)

course of irradiation; the EPR spectra of those radicals are described by different radiospectroscopic parameters; in addition, those radicals possess different thermal stabilities. The modifications of the spectral shape with the growing time of the isothermal annealing at a temperature of 130 °C are depicted in Fig. 3. After the long-term annealing (for more than 600 min), we observed that the intensity of the line related to SO_3^- radicals became reduced, and there emerged a line associated with SO_2^- radicals with the g-factors $g_1 = 2.0130$, $g_2 = 2.0035$, and $g3 = 2.01045$. This fact testifies that, in the course of the high-temperature annealing, barium dithionate transforms into barium sulfite [5]. The decay rate of SO_3^- radicals at the annealing depends on the annealing temperature and the exposure dose: the higher the temperature and the dose, the faster is the decay. Figure 4 illustrates, as an example, the dependences of the EPR spectrum amplitude on the annealing time at a temperature of 85 °C of powder specimens that were preliminarily irradiated with gamma rays up to the exposure doses of 10 (curve *1*) and 10^4 Gy (curve *2*).

T a b l e 2. Parameters used for simulating the complicated EPR spectrum obtained after the UV irradiation of crystalline barium dithionate dihydrate

Spectrum	Line shape	g	$g_\parallel$	$g_\perp$	ΔH_{pp}, mT
SO_3^-:$BaS_2O_6 \cdot 2H_2O$	Gaussian	2.0026			0.28
R_1, axial	Gaussian	2.0054			0.13
R_2, isotropic	Gaussian	2.0068	2.0085	1.7	
R_3, isotropic	Gaussian	2.000			0.13
R_4, isotropic	Gaussian	2.0054			1.38
SO_2^-:$BaSO_4$	Lorentzian	2.0130 (g_1)	2.0035 (g_2)	2.0104 (g_2)	
Cr^{3+} in MgO	Gaussian	1.98			0.28

From the experimental data presented above, it follows that, in the course of the gamma irradiation of powder specimens, there emerge the paramagnetic centers (radicals) of at least five different types; their EPR spectra are described by different halfwidths and g- and A-tensors.

When the powders of crystalline barium dithionate were irradiated with UV rays at room temperature and under the relative humidity of 40–80%, the observed EPR spectra turned out to be distinct from the spectra that were observed after the specimen irradiation with γ-quanta. In Fig. 5, the EPR spectrum of a powder specimen irradiated with UV rays from a PRK-4 medium pressure mercury tube is exhibited. The time of irradiation was 100 h. It should be noted that the shape of the EPR spectrum varied in the course of irradiation. The spectrum in Fig. 5 can be interpreted as such which includes the lines of SO_2^- radicals in $BaSO_4$ and the lines of SO_3^- radicals in $BaS_2O_6 \cdot 2H_2O$, as well as the unidentified lines R_1, R_2, R_3, and R_4. The radiospectroscopic parameters of all those spectra are listed in Table 2. It should be emphasized that the UV irradiation was carried on simultaneously for

a number of specimens of crystalline barium dithionate dihydrate, three of which were reference specimens. The first reference specimen was covered with a piece of ordinary pane glass, the second with a metal plate, and the third with a piece of silica glass. The specimens, which had been protected against UV irradiation (using an ordinary glass or a metal plate), did not reveal any emergence of paramagnetic centers, while the specimen covered with silica glass and the uncovered specimens showed the appearance of radicals which gave the EPR spectrum exhibited in Fig. 5. The researches of UV-irradiated barium dithionate testified that radicals of several types, including SO_3^- and SO_2^- ones, emerge in this case. The irradiation of barium dithionate specimens with UV rays was accompanied by their irradiation with infrared (IR) rays as well, which were present in the emission spectrum of PRK tubes; as a result, there occurred a thermal-radiation transformation of barium dithionate into another phase. It should also be noted that the irradiation with IR rays could result in the partial annealing of SO_3^- radicals, so that we would observe a reduced intensity of the EPR line of this radical.

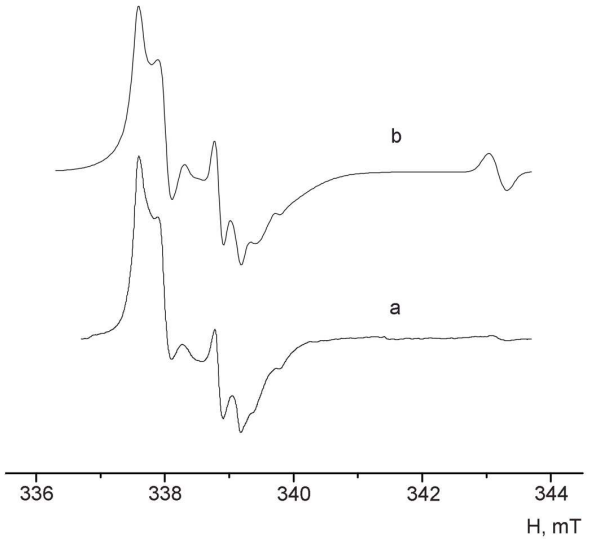

Fig. 5. EPR spectra of UV irradiated barium dithionate powder specimens: (a) theoretical simulation making use of the parameters quoted in Table 2, (b) experimental data ($\nu_{\rm UHF} = 9.511$ GHz)

4. Conclusions

The results obtained testify that, in the course of the gamma irradiation of powder specimens of crystalline barium dithionate dihydrate, the paramagnetic centers of various kinds and with different EPR characteristics are formed. The EPR lines of these centers become saturated at different UHF powers; they are characterized by different halfwidths and shapes, g- and A-tensors. We have identified SO_3^- centers in $BaS_2O_6 \cdot 2H_2O$ and SO_2^- ones in $BaSO_4$; other centers have not been identified. If powder specimens are irradiated with short-wave UV rays (without filters) using medium pressure mercury tubes (of the PRK-4 type), the paramagnetic centers of several types, including SO_3^- radicals, also emerge. A discrepancy between the g-factors of lines, which are observed in the EPR spectra of barium dithionate powders irradiated with γ- or UV rays, can be interpreted as the formation of radicals of different corresponding types. It is probable that the UV irradiation generates more radicals in the surface layers of the substance, while more radicals arise in the specimen bulk at γ-irradiation, so that their characteristics could be different. If barium dithionate is irradiated with the help of a PRK tube, SO_3^- radicals become partially annealed, and the lines of intermediate radicals, which arise in the course of the thermal-radiation transformation of barium dithionate into barium sulfite, may probably be observed. The elucidation of this issue demands additional researches.

It should also be emphasized, that if crystalline barium dithionate dihydrate is used as a material for EPR dosimetry, one should bear in mind that this substance, being subjected to γ-irradiation, demonstrates the EPR spectrum which consists of several lines with different parameters. Therefore, it is always necessary to maintain the identical conditions of spectrum registration, such as the UHF power, the amplitude and the modulation frequency of the magnetic field, the magnetic field scanning rate, and the Q-factor of the working cavity). It should also be taken into account that UV irradiation gives rise to the formation of various additional EPR centers including SO_3^- ones, which can influence the accuracy of the determination of the exposure dose.

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ЕПР РАДІАЦІЙНИХ ЦЕНТРІВ
У КРИСТАЛОГІДРАТІ ДИТІОНАТУ БАРІЮ

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Р е з ю м е

Методом ЕПР вивчено властивості порошкових зразків дитіонату барію, опромінених γ- і ультрафіолетовими (УФ) променями. Встановлено, що внаслідок гамма-опромінення в ньому утворюється принаймні п'ять радикалів, спектри яких описуються різними параметрами. Для двох з них визначено A-тензори, а саме для R_1 (SO_3^-) – $A_{zz} \approx A_{yy}$= 11,65 мТл, A_{xx} = 15,64 мТл; для R_2 – $A_{zz} \approx A_{yy}$= 10,3 мТл, $A_{xx} = 14,73$ мТл. Показано, що внаслідок короткохвильового УФ-опромінення в таких самих зразках утворюється кілька парамагнітних центрів, в тому числі радикали SO_3^-. В роботі визначено ЕПР-параметри цих центрів.