The Study of Radiolysis of $Ba(NO_3)_2$ by ESR

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Abstract. Irradiation of $Ba(NO_3)_2$ γ-rays at 308 K at increasing absorbed dose creates several new PC: 1, 2, 3, X. All of these are characterized by almost isotropic g-factor. Comparison of the observed parameters with literature data allows us to identify the PC as follows: 1 - O_3^-, 2 - O^-. PC 3 and X presumably attributed to the complex centers $[NO_2...O_2]$ or $[NO_2^-...O^-...O_2]$ and $[O^-...O_2]$, respectively.

1. Introduction

The paramagnetic centers (PC) NO_2, O_n^- (n = 1-3), and F-centers were found under the radiolysis of crystalline $Ba(NO_3)_2$ at 300 K [1, 2]. At 77 K PC NO_3, ONOO, and NO_3^{2-} were found [3-6]. The diamagnetic products peroxynitrite $ONOO^-$ and nitrite NO_2^- were formed by radiolysis of crystalline $Ba(NO_3)_2$ at 300 K [7-9].

X-ray irradiation at 300 K (absorbed dose ~ $5\cdot10^3$-$5\cdot10^4$ kGy was estimated by us from the data represented in [1]) results in ESR spectrum due to F-centers, O_2^-, O_3^-, and NO_2 [1]. The latter was registered at 85 K only. The annealing of F-centers was observed at room temperature, and at 358 K they completely decay within 3-5 minutes. This process simultaneously results in the increasing of O_2^- and O_3^- concentration.

A γ-ray irradiation at 300 K (absorbed dose ~ 1000 kGy) results in ESR spectrum due to O^-, O_3^-, and unidentified paramagnetic center [2]. The former is stable up to 570 K, the latter is annealed at 330-350 K. The ozonide ion decay under the heating of irradiated sample up to 440-480 K. Thus, there are the difference both PC observed in [5,6] and they thermal stability. It may be connected with the values of absorbed dose.

The goal of this investigation is to study the accumulation of PC under γ-irradiation of $Ba(NO_3)_2$ at 308 K.

2. Experimental

Single crystals of $Ba(NO_3)_2$ were grown by slow evaporation of aqueous solution of "reagent grade" salt. The samples were irradiated with ^{60}Co γ-rays at 308 K. The dose rate 0.69 Gy/s was measured with a Fricke dosimeter, assuming the radiation chemical yield of Fe^{3+} to be equal to 15.6 $(100\ eV)^{-1}$. The absorbed dose was calculated using the mass energy absorption coefficients. ESR spectra were registered by X-band spectrometer Bruker EMX Micro 6/1 at 300 K. The angular dependences of ESR spectra were constructed with using DPPH (g = 2.0036). The value of g-tensor were determinate with accuracy ± 0.0007.

3. Results

ESR spectrum due to all of observed PC was registered under irradiation by dose 400 kGy only (Fig. 1). Eigenvalues of PC' g-tensor represent in Table 1 were calculated from dependencies of the ESR spectra for different crystal orientation in the magnetic field. As seen, all of observed PC have almost isotropic g-tensors while in the earlier studies they have axial or rhombic symmetry (Table 1).

From our calculated g-factors values and published data it is follows that PC 1 is radical O_3^-, the PC 2 and PC X are radical O^-. A g-factor of PC 3 corresponds to radical NO_2, but its hyperfine structure differ from the one for NO_2 in other matrix. For the latter case, the assignment is clearly self-explanatory, because we observed only two from three lines (low intensity of spectrum is not possible to observe the remaining line) and the hyperfine splitting does not match the known values for this radical.

Irradiation by the doses from 10 to 150 kGy of barium nitrate single crystals results in the ESR spectrum due to ion-radical O_3^- only. It is stable at 300 K.

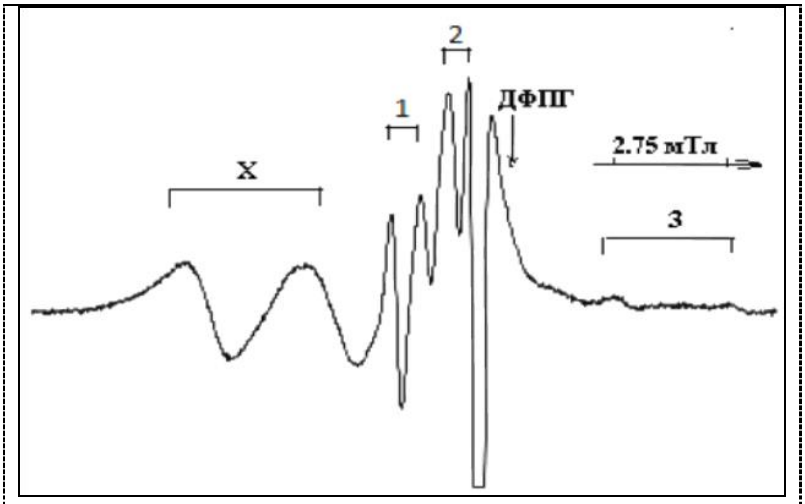

Figure 1. Spectrum ESR γ-irradiated (400 kGy) $Ba(NO_3)_2$.

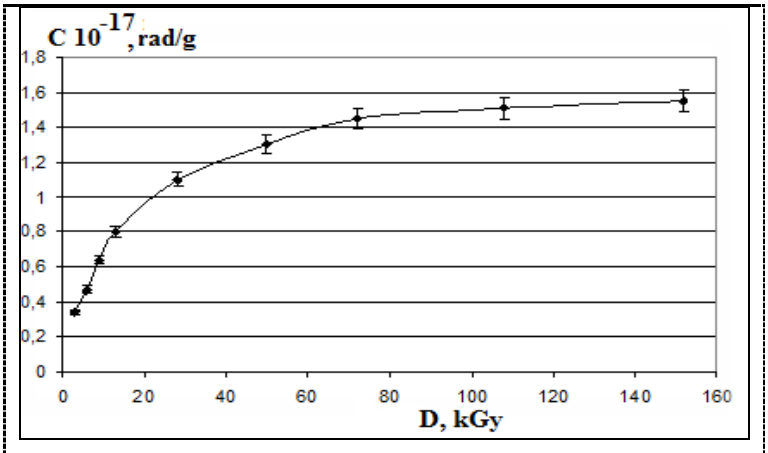

Figure 2. Accumulation radical O_3^- at γ-radiolysis of $Ba(NO_3)_2$.

Table 1

Eigenvalues of g- tensors for PC X, 1, 2, and 3.

Radical	g_{xx}	g_{yy}	g_{zz}	g_{ave}
X	2.0453	2.0448	2.0451	2.0451
1	2.0218	2.0170	2.0172	2.0190
2	2.0110	2.0107	2.0128	2.0115
3	1.9889	1.9798	1.9761	1.9816

The accumulation of O_3^- up to 15 kGy is almost linearly (Fig. 2). The value of initial radiation-chemical yield of O_3^- is equal to 0.016 rad/100 eV. Increase of the irradiation dose results in decrease of the rate of O_3^- formation and at the absorbed dose higher than 80-100 kGy the concentration become constant ($1.6\ 10^{17}$ rad/g).

Irradiation of barium nitrate by dose > 120 kGy results in ESR spectrum due to O^-, and when dose > 1400 kGy one can be see center X (Fig. 3). At dose > 350 kGy in the ESR spectrum appears two small signals assignment as 3 in Fig. 1. The increase of the absorbed dose results in the decrease of its rate of formation X, but the accumulation of the paramagnetic center observes up to ~ 500 kGy.

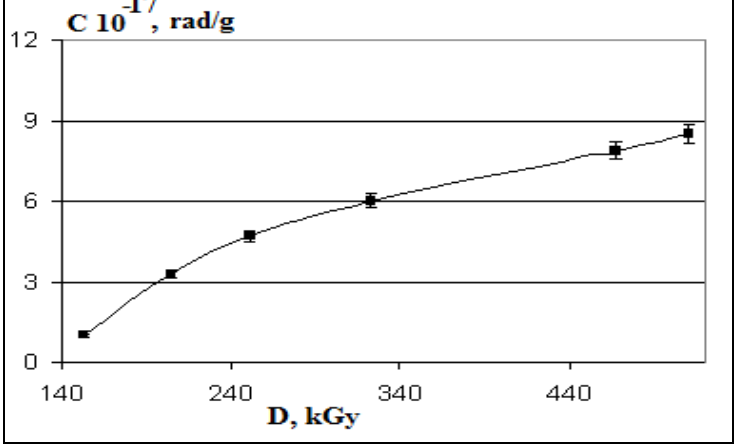

Figure 3. Accumulation radical X at γ-radiolysis of $Ba(NO_3)_2$.

The consistent irradiation of single crystal $Ba(NO_3)_2$ at 308 K to 40kGy and then at 77 to 1kGy result to appearance in ESR spectrum lines belonging to the radical NO2, located in four magnetically nonequivalent positions (Fig. 4).

4. Discussion

Comparison of the parameter of g-tensor observed radicals with literature data allows us to identify the PC as follows: 1 - O_3, 2 - O^-. PC 3 and X presumably attributed to the complex centers [O^- ... O_2] and [NO_2 ... O_2] or [NO_2^- ... O^- ... O_2], respectively.

At γ-irradiation is forming complex "cell" centers [NO_2^-...O] or [NO_2^-...O_2...NO_2^-]. It is supposed that initially analogical “cell” pairs are formed in the volume and on the surface of $Ba(NO_3)_2$ at photolysis [10] too.

The collapse of complex defects may result in the "free" radical O^-. Interaction O^- with a molecule of oxygen O_2 leads to O_3^-. Presumably, at low absorbed doses, is forming centers of the type [NO_2^- ...O_2...NO_2^-] and radicals are formed O_3^- only. Then, in the ESR spectra appear free radicals O^-.

Next capture free electrons and holes on the above-mentioned complex radiation defects can lead to radical products of transformation of these particles. Thus, paramagnetic particles can be formed from $[NO_2^-...O^-]$ or $[NO_2^-...O_2]$ to create free oxygen radicals or complex products, for example:

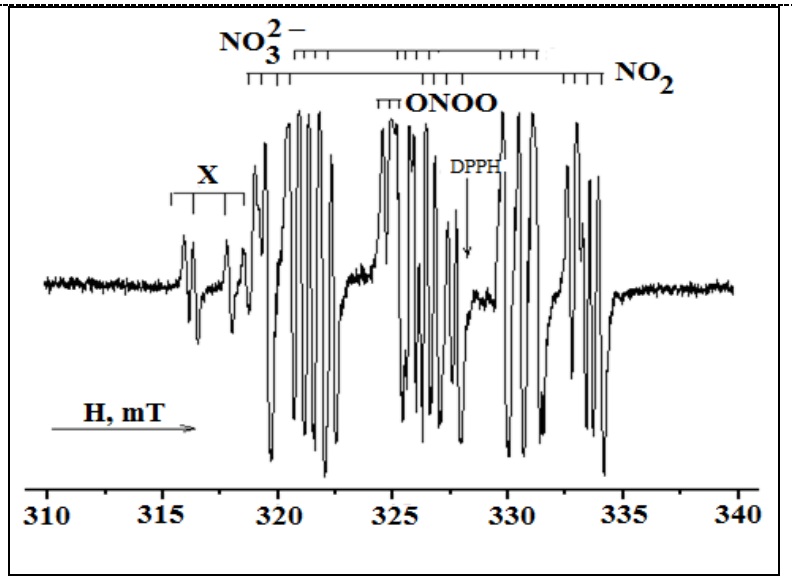

Figure. 4. The ESR spectrum of $Ba(NO_3)_2$ γ-irradiated at first at 300K (40 kGy) and then at 77 K (1 kGy), measured at 77K.

$$[NO_2^-\ldots O] + e \rightarrow NO_2^- + O^-$$
$$[NO_2^-\ldots O] + e \rightarrow [NO_2^-\ldots O^-]$$

Formation of simple paramagnetic centers O_n^- output due to the possibility of diffusion such a radical in the interstitial space.

$$[NO_2^-\ldots O_2] + O^- \rightarrow NO_2^- + O_3^-$$

Capture free holes can be result in formation radical NO_2

$$[NO_2^-\ldots O] + h \rightarrow NO_2 + O$$

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