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$_2$$_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 ~ 5-10$^3$-5-10$^4$ 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

<table>
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<tr>
<th>Radical</th>
<th>$g_{xx}$</th>
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<td>1.9798</td>
<td>1.9761</td>
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</tbody>
</table>

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 ($1.6 \times 10^{17}$ rad/g).

Irradiation of barium nitrate by dose > 120 kGy results in ESR spectrum due to $O_\cdot$, 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.

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 - $O_\cdot$. 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 $\gamma$-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 $O_\cdot$. Interaction $O_\cdot$ 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 $[\text{NO}_2^{-}...\text{O}^-]$ or $[\text{NO}_2^{-}...\text{O}_2]$ to create free oxygen radicals or complex products, for example:

$$[\text{NO}_2^{-}...\text{O}] + e \rightarrow \text{NO}_2^{-} + \text{O}^-$$

$$[\text{NO}_2^{-}...\text{O}^-] + e \rightarrow [\text{NO}_2^{-}...\text{O}^-]$$

Formation of simple paramagnetic centers $\text{O}_n^-$ output due to the possibility of diffusion such a radical in the interstitial space.

$$[\text{NO}_2^{-}...\text{O}_2] + \text{O}^- \rightarrow \text{NO}_2^{-} + \text{O}_3^-$$

Capture free holes can be result in formation radical $\text{NO}_2$

$$[\text{NO}_2^{-}...\text{O}] + h \rightarrow \text{NO}_2^{-} + \text{O}$$

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References