PARAMAGNETIC CENTERS FORMATION UNDER RADIOLYSIS OF CRYSTALLINE $RbNO_3$ AND $CsNO_3$

V. Anan'ev and V. Pak
Kemerovo State University, Krasnaya 6, Kemerovo, 650043, Russia

The goal of the present paper is to study the paramagnetic centers formation under γ-radiolysis of crystalline $RbNO_3$ and $CsNO_3$ at 300 K and their decay under the heating to develop the mechanism for radiolysis products formation.

The $RbNO_3$ and $CsNO_3$ crystals were irradiated with ^{60}Co γ-rays at ~ 310 K. The irradiated $RbNO_3$ and $CsNO_3$ crystals were thermal annealed at 393 K and 423 K, respectively.

$O^{\bullet -}$ and $NO_2^{\bullet}$ centers are registered in ESR spectra of irradiated crystals. The kinetics of $O^{\bullet -}$ accumulation has a nonlinear character, when for $NO_2^{\bullet}$ it is linear. The values of $O^{\bullet -}$ initial radiation chemical yield – $G(O^{\bullet -})$ are equal to 0.01 and 0.14 $(100\ eV)^{-1}$ for $RbNO_3$ and $CsNO_3$, respectively, when $G(NO_2^{\bullet})$ – 0.03 $(100\ eV)^{-1}$ for studied nitrates. The thermal annealing of irradiated samples results in the drop of the initial centers with simultaneously appearance of the $O_3^{\bullet -}$, but not $O_2^{\bullet -}$.

The initial product of radiolysis of the nitrates is the complex $[xNO_2^- \ldots O_x]$. Because $O_3^{\bullet -}$ formation from $O^{\bullet -}$ under thermal annealing is possible if the molecular oxygen formed under irradiation only, then x = 2. Therefore $O^{\bullet -}$ formation is not due to the localization of the electron on the atomic oxygen of the complex. The complex $[NO_2^{\bullet} \ldots O^{\bullet -}]$ may be formed under the dissociation of the excited nitrate ion formed under irradiation. Hence, the formation of that complex in crystalline nitrates is at variance to the fact that $G(O^{\bullet -})$ disagree with $G(NO_2^{\bullet})$.

The mechanism for the paramagnetic centres formation under the radiolysis of $RbNO_3$ and $CsNO_3$ crystals and the heating can be written as follows.

Under irradiation: $NO_3^- + e \rightarrow NO_3^{\bullet 2-} \rightarrow [NO_2^- \ldots O^{\bullet -}]$; $2NO_3^- + h \rightarrow (NO_3)_2^{\bullet -} \rightarrow [NO_2^{\bullet} \ldots O_2 \ldots NO_2^-]$

Under the heating: $[NO_2^{\bullet} \ldots O_2 \ldots NO_2^-] \rightarrow [NO_2^{\bullet} \ldots NO_2^-] + O_2$; $O_2 + [NO_2^- \ldots O^{\bullet -}] \rightarrow [NO_2^- \ldots O_3^{\bullet -}]$

Acknowledgements: This research was conducted with financial support from Federal Target Programme "Scientific&Scientific-Pedagogic Manpower of Innovation Russia" 2009-2013 years.