The Radiation Decomposition of Crystalline Alkali Nitrates

V.A. Anan'ev, M.N. Seliverstov

Kemerovo State University, Krasnaya str., 6, Kemerovo, 650043, Russia. E-mail: eprlab@kemsu.ru

Abstract – The kinetics of peroxynitrite accumulation in alkali nitrate crystals γ – irradiated at 310 K has been studied. The mechanism of radiolysis of crystalline alkali nitrates are assumed to be connected with the formation of the peroxynitrite ions and the nitrite ions due to decay of high – energy singlet and triplet molecular excitons respectively. These excitons can be generating under the relaxation of electrons from the anion conductivity band to the anion conductivity band accompanied by the Auger excitation of the nitrate ions to the E' states.

1. Introduction

In crystalline alkali nitrates the peroxynitrite ion $(ONOO^-)$ is initial defect which contributes much to the formation of final products of UV – irradiation of solid potassium nitrate – nitrite and oxygen [1]. The peroxynitrite formation is supposed to occur under the radiolysis of nitrates, however, this assumption is based on the chemical analysis data obtained after the dissolution of irradiated samples [2].

The goal of the present paper is to analyse the optical spectra of γ – irradiated alkali nitrate crystals to determine the efficiency of peroxynitrite formation in solid state and to find out whether the peroxynitrite ion is the initial radiation defect whose dissociation results in the nitrite ion or not.

2. Experimental

Alkali nitrate crystals, both pure and doped, were grown by slow evaporation of saturated aqueous solutions. The nitrates and the nitrites used were a.r. grade (three times crystallized from redistilled water before use). The nitrite ions were introduced into the alkali nitrate solutions in the form of corresponding nitrite salts. A typical dimension of the samples was 1×0.5 cm and their thickness varied from 0.004 to 0.200 cm.

The procedure for the chemical analysis of nitrite was described earlier [3].

The crystals were continuously irradiated with ^{60}Co γ – rays on an RChM – γ – 20 source at ~ 310 K. The dose rate (0.8 – 2.5) Gy/s was measured with a Fricke dosimeter, assuming the radiation yield of Fe^{3+} to be equal to 15.6 $(100\ eV)^{-1}$. The dose absorbed by the sample was calculated using the mass energy absorption coefficients.

The thermal annealing of γ – irradiated $RbNO_3$ and $CsNO_3$ crystals was carried out at 120 ^{O}C (the accuracy was ±1 ^{O}C). The nitrite formation in non – irradiated crystals was not observed at this temperature.

The optical absorption spectra of single crystals were measured on "SPECORD UV – VIS" spectro-photometer at room temperature. An analysing non – polarized light beam was directed perpendicularly to growth sides of $RbNO_3$ and $CsNO_3$ crystals, to the cleavage fracture of $NaNO_3$ crystal and parallel to the crystallographic z – axis of KNO_3 crystal. The radiation – induced optical absorption in all crystals is of an isotropic character in the long – wavelength region (>320 nm). To increase the reliability of the data 3 – 5 crystals of each alkali nitrate were studied.

3. Results

The efficiency of nitrite formation in γ – irradiated crystalline alkali nitrates were studied in the dose range 3 – 300 kGy. It has been found that nitrite increases with doses linearly. Its radiation chemical yield is equal to 0.21, 1.57, 0.61, 1.61 $(100\ eV)^{-1}$ for $NaNO_3$, KNO_3, $RbNO_3$ and $CsNO_3$ respectively. These values are in good agreement with the published data.

Fig. 1 displays the optical spectra of $RbNO_3$ and $CsNO_3$ crystals doped with the nitrite ions introduced by co – crystallization. An additional absorption band (the maximum at 358 nm and the half – widths 3100 and 3800 cm^{-1} in $RbNO_3$ and $CsNO_3$ crystals respectively) appears in the spectra of doped crystals compared with the spectra of pure nitrate crystals (Fig. 2, curve 1).

As seen, a vibrational band structure with clearly separated peaks due to the nitrite ions is observed in the long – wavelength edge of the band. The vibration frequencies for the nitrite ion v_1' and v_2'' in the B_1 state are equal to 1020 and 630 cm^{-1} respectively in the $NaNO_2$ crystal [4], which is in good agreement with the data represented in Fig. 1.
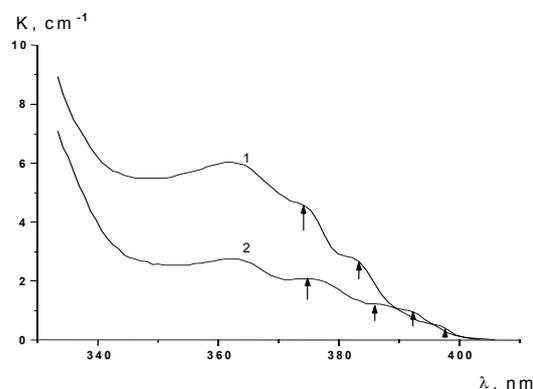
Fig. 1. Absorption spectra of $RbNO_3$ (1) and $CsNO_3$ (2) crystals doped with nitrite (the concentration – 0.74 and 1.42 mol.% respectively)
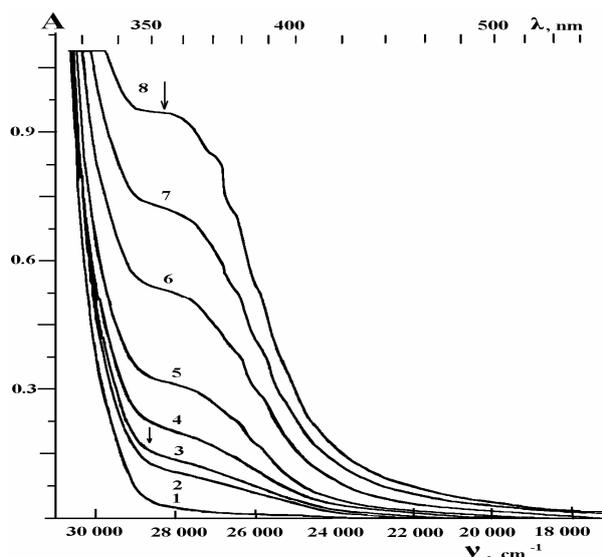
Fig. 2. Absorption spectra of $CsNO_3$ crystal with thickness 0.070 cm γ – irradiated with the doses 0, 0.5, 3.2, 9.5, 22.3, 38.1, 54.0 and 79.5 kGy – 1, 2, 3, 4, 5, 6, 7 and 8 respectively

An absorption band without a vibrational structure due to nitrite introduced by co – crystallization into sodium and potassium nitrate crystals (the maximum at 351 and 360 nm, the half – widths 3100 and 3800 cm^{-1} in $NaNO_3$ and KNO_3 crystals respectively) appears in the long – wavelength region of the spectra of doped crystals.

From the data of the chemical analysis and optical measurements it follows that molar absorptivity of nitrite is equal to 15.5, 13.1, 32.5 and 10.5 $M^{-1}cm^{-1}$ for $NaNO_3$, KNO_3, $RbNO_3$ and $CsNO_3$ crystals respectively.

The evolution of the absorption spectrum of the starting $CsNO_3$ crystal with thickness 0.070 cm to the intermediate products of radiolysis is shown in Fig. 2 (the absorption spectra of $RbNO_3$ crystals are almost the same). The absorbed dose increase brings about the qualitative change of the spectrum shape. The maximum of the spectrum at low absorbed doses is at 343 and 349 nm for $RbNO_3$ and $CsNO_3$ crystals respectively. At higher absorbed doses the maximum is shifted towards the long – wavelength region (in Fig. 2 the maximum at different absorbed doses is shown with arrows), while in the spectrum there appears the vibrational structure caused by the nitrite ions.

Fig. 3 displays the spectrum of the γ – irradiated $CsNO_3$ crystal thermal annealed for 1.5 h. The annealing results in the drop of absorption intensity between 320 – 410 nm with a simultaneous appearance of a wide band with its maximum at 450 nm. Analogous results have been obtained for $RbNO_3$ crystal.

The comparison of the parameters of the band in a short – wavelength region (Fig. 3) with those caused by the nitrite ions in doped nitrate crystals (Fig. 1) shows that after thermal annealing the spectrum is caused by the nitrite ions and the ozonide ions. The

presence of the ozonide ions is proved by the ESR data [5]. Molar absorptivity of nitrite in annealed crystals is equal to 350 and 150 $M^{-1}cm^{-1}$ for $RbNO_3$ and $CsNO_3$ crystals respectively, which is ten times higher than for nitrite introduced by co – crystallization. It may be assumed that this difference is due to the formation of the complexes consisting of the nitrite ion and an oxygen atom or molecule under irradiation.
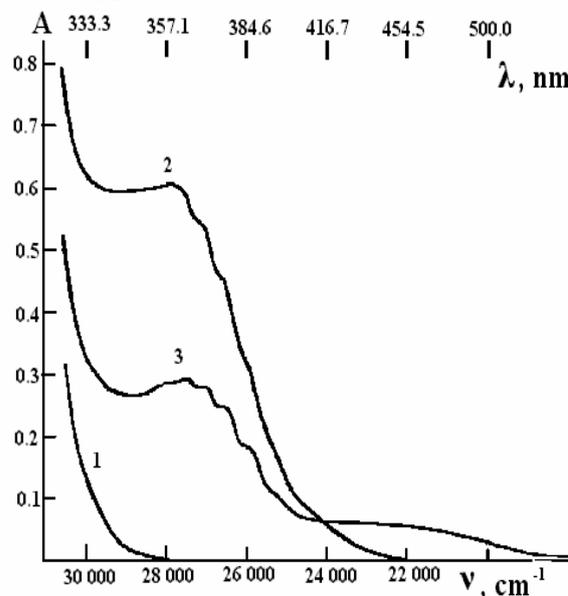
Fig. 3. Absorption spectra of $CsNO_3$ crystal. 1 – untreated. 2 – γ – irradiated. 3. Same as 2, annealed 1.5 hr at 100 ^{0}C

Based on the chemical analysis data it follows that the annealing of γ – irradiated crystals under the above conditions results in the 7 and 5 % drop of the concentration of nitrite in irradiated $RbNO_3$ and $CsNO_3$ crystals respectively.

As it is known, the thermal annealing of peroxynitrite produced by UV – irradiation of $RbNO_3$ and $CsNO_3$ crystals is responsible for the complete decay of peroxynitrite [6], therefore, the spectrum (difference spectrum) which has been calculated as the difference between γ – induced spectra before and after annealing (taking into account the bands of both the ozonide ions and the nitrite ions annealed by heating) has been analyzed. It turned out to be described only by a single band with the following parameters: the band maximum – at 343 and 349 nm; the half – width – 5550 and 5450 cm^{-1} for $RbNO_3$ and $CsNO_3$ crystals respectively. The same parameters belong to low – energy band caused by peroxynitrite in the UV – irradiated $RbNO_3$ and $CsNO_3$ crystals [6]. The results obtained prove that peroxynitrite can be formed in irradiated alkali nitrates in solid state.

From the data on the difference spectra in the γ – irradiation $RbNO_3$ and $CsNO_3$ crystals and peroxynitrite molar absorptivity in the UV – irradiated crystals (3800 (343 nm) and 7100 $M^{-1}cm^{-1}$ (349 nm) for

RbNO$_3$ and CsNO$_3$ respectively), we calculated the peroxynitrite buildup kinetics, which is shown in Fig. 4.

A single absorption band appeared in the long – wavelength region of the absorption spectrum of NaNO$_3$ and KNO$_3$ crystals γ – irradiated to a small dose. The maximum position (at 341 and 349 nm) and the half – width (4200 and 5750 cm^{-1} for NaNO$_3$ and KNO$_3$ crystals respectively) of this absorption band allowed us to state that this was due to peroxynitrite [7].
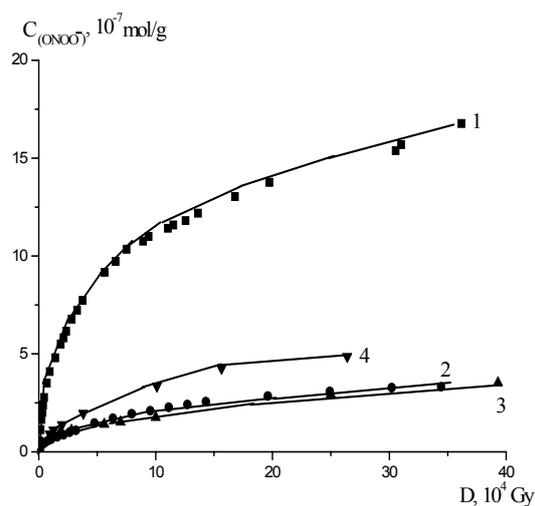
Fig. 4. The curves of peroxynitrite accumulation vs. absorbed doses for alkali nitrates (1, 2, 3 and 4 – NaNO$_3$, KNO$_3$, RbNO$_3$ and CsNO$_3$ respectively)

From the data on absorbance rise at 341 nm (NaNO$_3$) and 349 nm (KNO$_3$) in the γ – irradiated crystals and peroxynitrite molar absorptivity in the UV – irradiated crystals (1000 (341 nm) and 3600 (349 nm) M^{-1}cm^{-1} for NaNO$_3$ and KNO$_3$ respectively [7]), we calculated the peroxynitrite buildup kinetics, which is shown in Fig. 4. In the calculations of peroxynitrite concentrations in the irradiated samples, we took into account that the accumulation of nitrite formed under radiolysis should be linear. The values of initial peroxynitrite radiation yield in the crystalline alkali nitrates were calculated on an initial linear part of accumulation curves. They are equal to 0.6, 0.14, 0.35 and 0.65 (100 eV)$^{-1}$ for NaNO$_3$, KNO$_3$, RbNO$_3$ and CsNO$_3$ respectively. Thus, the values of initial radiation yield of nitrite are large than the ones of peroxynitrite in solid KNO$_3$, RbNO$_3$ and CsNO$_3$.

4. Discussion

It is stated that the products of radiolysis of NaNO$_3$ and KNO$_3$ irradiated at 77 K are localized charges with the initial radiation yield of localized hole centers NO$_3$ being ~ 13 and 11 (100 eV)$^{-1}$ respectively [8]. Taking into account the fact that the band gap E$_g$ (from the top of the valence band to the bottom of the cation conductivity band) for all nitrates is ~8 eV [9],

it can be assumed that the irradiation energy is practically entirely utilized on the formation of charges. Therefore, it is reasonable to assume that the formation of diamagnetic radiolysis products occurs through the decay of excitons that are formed in the interaction of paramagnetic centers with each other [10]. However, findings that conflict with this assumption have been reported recently. On the basis of the pulse radiolysis data on alkali metal nitrates, it was established that peroxynitrite has the same time of formation as paramagnetic centers [11]. Furthermore, the decay of the latter species, which are generated by irradiation at both 83 [12] and 300 K [11], does not affect optical absorbance due to peroxynitrite. From these facts, it follows that the generation of excitons and electron – hole pairs during radiolysis can occur independently of one another.

Let us assume that the efficiencies of peroxynitrite formation by 253.7 – nm photolysis and in the decay of excitons generated by radiolysis are equal. Based on the values of peroxynitrite quantum yield (0.024, 0.055, 0.061 and 0.064 quantum^{-1} for NaNO$_3$, KNO$_3$, RbNO$_3$ and CsNO$_3$ respectively [13]) under photolysis of alkali nitrates, it follows that the radiation – chemical yield of excitons under radiolysis of crystalline alkali nitrates will be equal to 20, 3, 6 and 10 (100 eV)$^{-1}$ for NaNO$_3$, KNO$_3$, RbNO$_3$ and CsNO$_3$ respectively.

Evidently, the energy required for the formation of paramagnetic and diamagnetic products of crystalline alkali nitrates radiolysis is inconsistent with the band – gap energy.

This fact can be explained based on the band structure in crystalline nitrates. A special feature of this structure consists in the both the narrow valence bands and the discontinuity of the spectrum of the vacant state [9]. The first band of the vacant states is mainly of an anion nature, while the second is of a cation nature [14] (the anion conductivity band and the cation conductivity band respectively). The maxima in electron state densities corresponding to these bands are in the 4 and 10 eV regions respectively, if the energy of the last occupied state is assumed to be zero.

Fig. 5 displays the structure of energy bands dealing with a sodium nitrate crystal and the correlation of the maxima in electron state densities [14] to molecular orbitals of the nitrate ion due to the calculations in [15]. For other alkali nitrate crystals the location of bands can be shifted as much as 0.5 eV [14]. Excitons (< 6 eV) formed under the irradiation of crystalline alkali nitrates are localized on separate nitrate ions which can be considered as molecular excited states of the nitrate ion.

Thus, the initial stage of the radiolysis of crystalline alkali nitrates results in the charges with holes in valence band and electrons in the cation conductivity band. An electron from this band can relax to the an-

ion conductivity band to generate ~5 – 6 eV accompanied by the Auger excitation of the nitrate ion to the high – energy excited $E^/$ state. In this case, the energy of this exciton can be somewhat higher than that of the exciton formed in 253.7 – nm photolysis. Triplet high – energy excitons can dissociate to form the nitrite ions and singlet ones can be transformed to form the peroxynitrite ions. The latter process is similar to the one observed under the photolysis (253.7 nm) of crystalline alkali nitrates [6]. Assuming that the values of quantum yield of peroxynitrite increases with exciton energy, we can explain its experimentally observed values of peroxynitrite radiation – chemical yield.
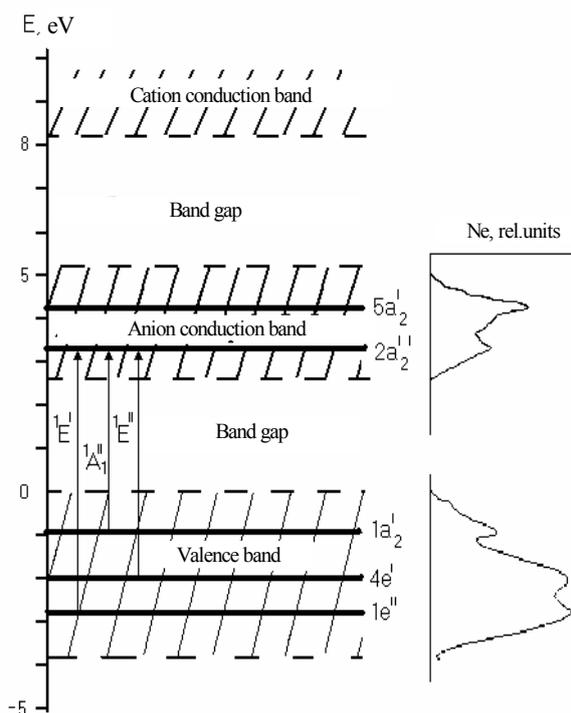
Fig. 5. Energy of band states of crystalline nitrates [15] (left), transitions between the ground states and excited states of free nitrate ion (left), density of higher valence band and anion conductivity band states (right) [14]

Based on the values of initial radiation yield of nitrite and peroxynitrite it can be stated that the major part of the former is not formed under the dissociation of the latter.

An electron from the anion conductivity band reacts with a hole from the valence band to form low – energy states of the nitrate ion (< 4 eV), the formation of the latter can also be due to the relaxation of the high – energy states.

At 77 K the electrons from the anion conductivity band and the holes from the valence band can be localized to form electron (NO_3^{2-}) and hole (NO_3) paramagnetic centers respectively. The NO_3^{2-} and NO_3

radicals undergo tunneling recombination to regenerate matrix nitrate ions [16].

5. Conclusion

The peculiarities of the formation of defects under the radiolysis of ion – molecular crystals (for example, alkali nitrate crystals) can be accounted for by the presence of the anion conductivity band and the energy of the generated excited states of a complex ion during the relaxation of electrons from the cation – into the anion conductivity band. If this energy is sufficient enough, it may be assumed that the defects due to the dissociation or transformation of the complex ion can also be formed under the radiolysis of some other ion – molecular crystals. Depending on the energy of the excitons the transformation of a complex ion to form various radiation point defects becomes possible.

References

[1] R.C.Plumb and J.O.Edwards. J. Phys. Chem. 96, 3245 (1992).
[2] V. Anan'ev, L. Kriger, M. Poroshina. Chem. Phys. Letters 362, 554 (2002).
[3] M. Miklin, L. Kriger, V. Anan'ev, V. Nevostruev. Chim. Visok. Energ. (Rus). 25, 506 (1989).
[4] Hangyo M., Yamanaka H. and Kato R. J. Phys. Soc. Japan. 50, 895 (1981).
[5] Anan'ev V., in: Proc. *12th Int. Conf. on Radiation Physics and Chemistry of Inorganic Material,* 2003 pp.128 – 130.
[6] V. Anan'ev, M. Miklin, N. Nelubina, M. Poroshina. Photochemistry & Photobiology A. Chemistry. 162, 67 (2004).
[7] V. Anan'ev, V. Vlaskin, M. Miklin, L. Kriger. Chim. Vys. Energ. (Rus) 31, 114 (1997).
[8] V. Anan'ev, S. Bannov, R. Khaliullin. Nucl. Instr. & Methods B. 191, 59 (2002).
[9] Y. N. Guravlev, V. A. Nevostruev, A. S. Poplavnoy. Chem.Phys. (Rus). 9, 1548 (1990).
[10] E. R. Johnson, *The Radiation – Induced Decomposition of Inorganic Molecular Ions,* New York – London – Paris, Gordon & Breach Sci. Pub., 1970, pp.33 – 85.
[11] Yu. N. Safonov, V. S. Dolganov, *High Power Pulse Beam in Technology,* Novosibirsk, Nauka, 1983, pp.81 – 102.
[12] P. Pringsheim. J. Chem. Phys. 23, 369 (1955).
[13] V. Anan'ev, M. Miklin. J. Photochem. & Photobiol. A: Chem. 172, 289 (2005).
[14] Y. Guravlev and A. Poplavnoy. Izv. Vuzov, Physics (Rus) 4, 51 (2001).
[15] V. A. Nevostruev. Izv. AN Latv. SSR. Ser. Phys. and Tech. Nauk. 5, 81 (1987)
[16] V. H. Pak and V. A. Nevostruev. Chim. Vys. Energ. (Rus) 34, 289 (2000).