TRANSFORMATION OF NITRATE ION INTO PEROXIDE UNDER IRRADIATION

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Different types of point defects formed in ion-molecular crystals have been described. Based on the data on radiation-induced optical spectra of alkali nitrate crystals peroxynitrite was stated to be one of these defects. The peculiarities of the formation of defects in ion-molecular crystals have been interpreted in relation to the structure of energy bands of these crystals.

INTRODUCTION

Extensive experimental data on the processes resulting in point defects in irradiated inorganic crystals are available now. Some of them deal with the defects genetically caused by biographical defects (vacancies, interstitial ions and impurity ions) others deal with point defects in a perfect irradiated crystalline lattice. Further, it is the latter case which is dealt with.

Let us consider the case when a regular site of the corresponding sublattice occupies atoms of one element. The crystal may be binary ionic (e.g. alkali halides) or covalent (e.g. non-metal oxides) due to the type of chemical bonds between sites. Both theoretical and experimental data available allow us to foresee what kind of point defects can be formed in these compounds under irradiation. The defects resulting from the removal of the ion from its site, e.g. both V_k-centres (a hole localized on two anions) together with F-centres (an electron localized on anion vacancies) and Frenkel defects in an anion sublattice are formed under the γ-irradiation of alkali halides [1]. The formation of point defects in covalent crystals is due to the localization of the charge on the single site. Thus, the classification of crystals into ionic and covalent stands to reason as the formation of point defects in the former crystals is due to the removal of an anion from the site into the interstitial, while in the latter-to the change of the charge of the site accompanied by an insignificant relaxation of neighbouring ions.

And now let us consider the crystals in which a regular sublattice site occupies a complex ion (the bond in the former crystals between regular sites is ionic but in the complex ion it is covalent). The analysis of the data available enables one to state that the formation of point defects in the above crystals is related to

1) the localization of the charge on two neighbouring anion sites (for instance, $(ClO_4)_2^-$ [2]) with an insignificant removal of anions from the regular sites;
2) the localization of the charges on anion sites (for instance, NO_3 or NO_3^{2-} [3]) to form electron and hole paramagnetic centres;
3) the dissociation of a complex ion involving the change of its structure with the conservation of an initial charge (for instance $[ClO^- \ldots O_2]$ [4]) or without it (for instance, $[ClO_2 \ldots O_2]$ or $[ClO_3^- \ldots O^-]$ [5]).

Thus, the type of point defects in ionic crystals with complex ions does not correspond to the type of point defects in either binary ionic or covalent crystals. That is why the ionic crystals with complex ions may be referred to as ion-molecular crystals.

All the papers concerning the radiolysis of ion-molecular crystals deal only with experimental registration of the defects. At the same time particular defects can be registered only at low temperature. It is evident that the lack of information on the kind of point defects in any ion-molecular crystals under irradiation does not allow us to suggest the mechanism for its radiolysis.

Although no other defects being formed in ion-molecular crystals under γ-irradiation are found, the formation of some other defects due to the transformation of the complex ion with the charge of the site

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unchanged but with the structure of covalent bonds in the complex ion without its dissociation being changed cannot be excluded. In crystalline alkali nitrates actually the peroxynitrite ion ($ONOO^-$), an isomer of nitrate ion, can be the defect contributing much to the formation of final products of UV-irradiation-nitrite and oxygen [6]. The peroxynitrite is supposed to be formed under the radiolysis of nitrates, however, this assumption is based on the chemical analysis data obtained after the dissolution of irradiated samples [7]. But according to the IR-spectroscopy data peroxynitrite is not registered in irradiated crystalline alkali nitrates [8]. To suggest the mechanism for radiolysis of nitrates it is important to find out whether the peroxynitrite ion is the initial radiation defect whose dissociation results in nitrite ion or not.

The goal of the present paper is to analyse the optical spectra of γ-irradiated alkali nitrate crystals to determine the formation of peroxynitrite in solid state.

EXPERIMENTAL

All chemicals used were analytical reagent grade or better. Cesium and rubidium nitrate crystals both pure and doped with nitrite ions were grown by slow evaporation of saturated aqueous solutions. Nitrite ions were added to nitrate solutions in the form of the 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 [9].

The crystals were continuously irradiated with ^{60}Co γ-rays at ~ 310 K. The dose rate 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 irradiated samples before use were stored at room temperature for 30 min.

The thermal annealing of γ-irradiated crystals was carried out in the thermostat at 80 and 100°C for $RbNO_3$ and $CsNO_3$ crystals respectively (the accuracy was ±1°C). Nitrite formation in non-irradiated crystals was not observed at this temperature.

The optical absorption spectra of single crystals were measured at room temperature. The optical absorption in $RbNO_3$ and $CsNO_3$ crystals is of an isotropic character. To increase the reliability of the data 3-5 crystals of each alkali nitrate were studied.

RESULTS

Figure 1 displays the optical spectra of rubidium and cesium nitrate crystals doped with 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 rubidium and cesium nitrate crystals respectively) appears in the spectra of doped crystals compared with the spectra of pure nitrate crystals (figure 2). As seen, a vibrational band structure with clearly separated peaks due to nitrite ions is observed in the long-wavelength edge of the band. The vibration frequencies for nitrite ion $\nu_1^{\prime}$ and $\nu_2^{\prime\prime}$ in the B_1 state are equal to 1020 and 630 cm^{-1} respectively in the $NaNO_2$ crystal [10], which is in good agreement with the data represented in figure 1.

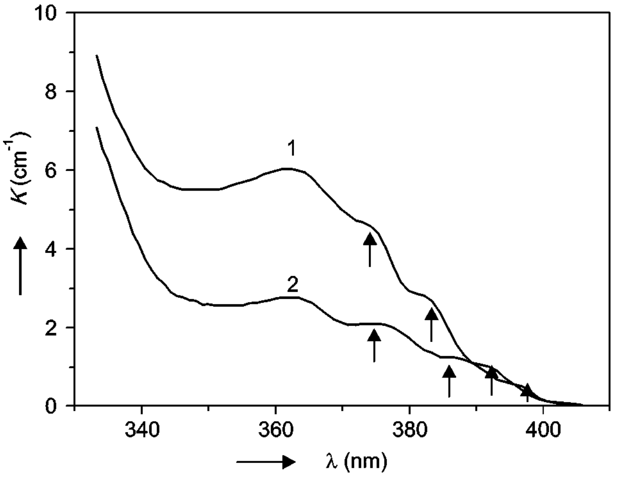

Figure 1. Absorption spectra of $RbNO_3$ (1) and $CsNO_3$ (2) crystals doped with nitrite, 0.74 and 1.42 mol.%, respectively.

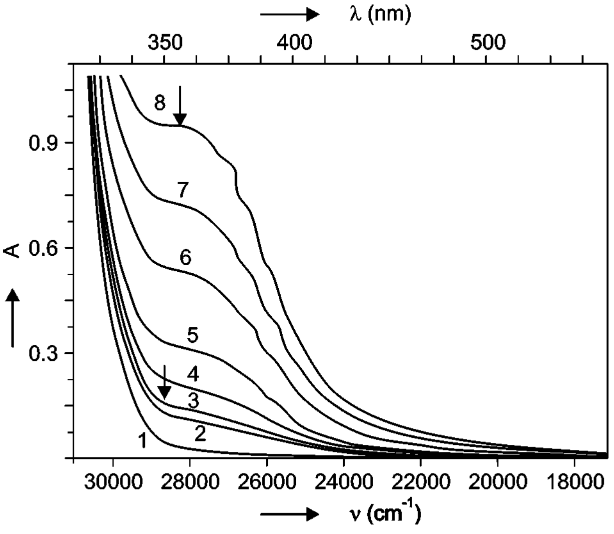

Figure 2. Absorption spectra of $CsNO_3$ crystal with thickness 0.070 cm γ-irradiated with the doses 0, 0.5, 3.2, 9.5, 22.3, 38.1, 54.0 and 79.5 kGy 1, 2, 3, 4, 5, 6, 7 and 8, respectively.

From the data of the chemical analysis and optical measurements it follows that molar absorptivity of nitrite is equal to 32.5 and 10.5 M^{-1} cm^{-1} for rubidium and cesium nitrate 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 figure 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 rubidium and cesium nitrate crystals respectively. At higher absorbed doses the maximum is shifted towards the long-wave region (in figure 2 the maximum at different absorbed doses is shown with arrows), while in the long-wavelength edge of the spectrum there appears the vibrational structure caused by nitrite ions.

Figure 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-wave region (figure 3) with those caused by nitrite ions in doped nitrate crystals (figure 1) shows that after thermal annealing the spectrum is caused by nitrite and ozonide ions. The presence of ozonide ions is proved by the ESR data [11]. Molar absorptivity of nitrite in annealed crystals is equal to 350 and 150 M^{-1} cm^{-1} for rubidium and cesium nitrate 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 nitrite ion and an oxygen atom or molecule under irradiation.

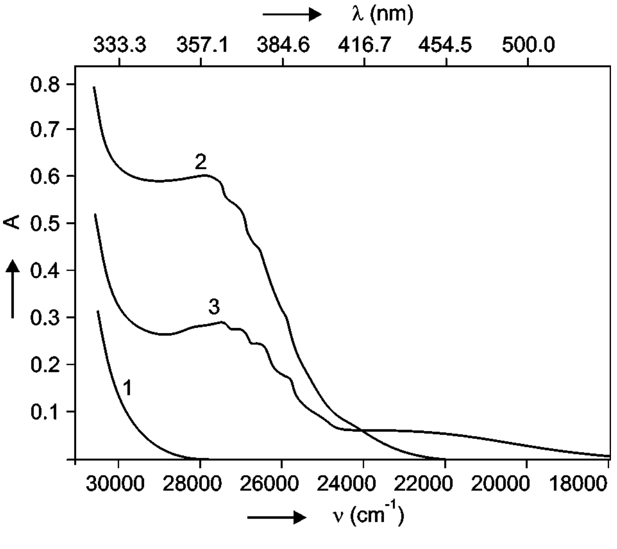

Figure 3. Absorption spectra of $CsNO_3$ crystal. 1-untreated. 2- γ-irradiated. 3. Same as 2, annealed 1.5 h at 100°C.

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 samples for rubidium and cesium nitrates respectively.

As is known, the thermal annealing of peroxynitrite produced by UV-irradiation of rubidium and cesium nitrate crystals is responsible for the complete decay of peroxynitrite [12], therefore, the spectrum which has been calculated as the difference between γ-induced spectra before and after annealing (taking into account the bands of both ozonide ions and 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 rubidium and cesium nitrate crystals respectively. The same parameters belong to low-energy band caused by peroxynitrite in the UV-irradiated rubidium and cesium nitrate crystals [12]. The results obtained prove that peroxynitrite can be formed in irradiated alkali nitrates in solid state.

Based on peroxynitrite accumulation data and its molar absorptivity in the UV-irradiated nitrate crystals [13], the initial radiation yield of peroxynitrite in γ-irradiated samples was estimated. It was equal to 0.34 and 0.65 $(100\ eV)^{-1}$ for rubidium and cesium nitrate respectively. Thus, the initial radiation yields of nitrite [3] are twice as large than the ones of peroxynitrite.

DISCUSSION

Different mechanisms for the formation of defects under the irradiation of ion-molecular crystals (for instance, crystalline nitrates) compared with binary ionic crystals can be due to the structure of energy bands characterized by both the narrow valence bands and the discontinuity of the spectrum of the vacant state [14]. The first band of the vacant states is mainly of an anion nature, while the second is of a cation nature [15] (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. Figure 4 displays the structure of energy bands dealing with a rubidium nitrate crystal and the correlation of the maxima in electron state densities [15] to molecular orbitals of nitrate ion due to the calculations in [16]. For other alkali nitrate crystals the location of bands can be shifted as much as 0.5 eV. 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 nitrate ion.

It is stated that the products of radiolysis of sodium and potassium nitrates irradiated at 77 K are localized charges with the initial radiation yield of localized hole centres NO_3 being ~ 13 and 11 $(100\ eV)^{-1}$ respectively [17]. 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 [14], it can be assumed that the irradiation energy is practically entirely utilized on the formation of charges. 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 anion conductivity band to generate ~5-6 eV. The energy can be consumed to form a high-energy excited state of nitrate ion (~5 eV). Triplet high-energy excited states of nitrate ion can dissociate to form 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 [12]. Based on the initial radiation yields of nitrite and peroxynitrite it can be stated that the major part of the former is not formed under the dissociation of the latter.

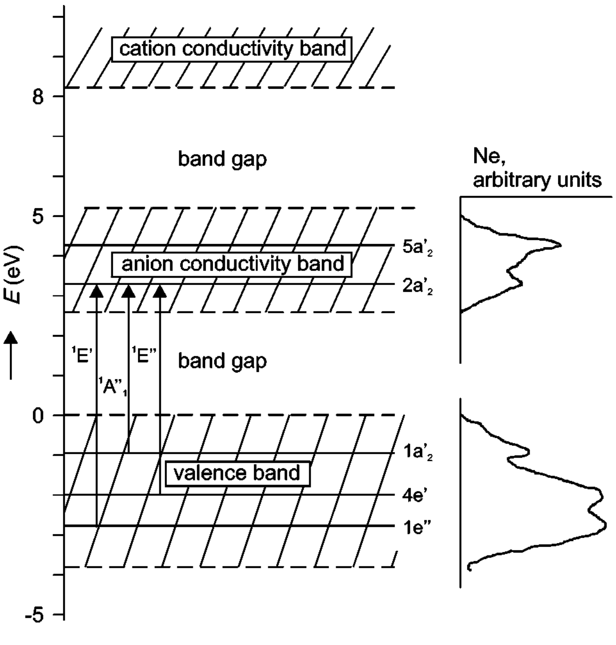

Figure 4. Energy of band states of crystalline alkali nitrates [16] (left), transitions between the ground states and excited states of free nitrate ion (left), density of higher valence band and anion conductivity band states (right) [16].

An electron from the anion conductivity band reacts with a hole from the valence band to form low-energy states of 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 and hole paramagnetic centres respectively.

CONCLUSIONS

The peculiarities of the formation of defects under the radiolysis of ion-molecular 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 (in addition to the ones considered in the paper) ion-molecular crystals. Depending on the energy of the excitons, the transformation of a complex ion to form various radiation point defects becomes possible.

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TRANSFORMACE DUSIČNANU NA PEROXID PO OZÁŘENÍ

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Jsou známy různé druhy bodových defektů, které se tvoří v iontově molekulových krystalech. Na základě optických spekter krystalů dusičnanů alkalických kovů ovlivněných ozářením tvrdíme, že jedním z těchto defektů je peroxodusitanový ion. Zvláštnosti vzniku defektů v iontově molekulárních krystalech jsme vysvětlili pomocí jejich pásové elektronické struktury.