The X-ray Radiolysis of Potassium Nitrate

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Abstract – The optical spectra irradiated single crystal potassium nitrate at 300 K were investigated. Kinetics of accumulation nitrite and peroxynitrite has been obtained. Nitrite ion, as shown, is secondary product of radiolysis of potassium nitrate.

1. Introduction

The radiation-induced decomposition of crystalline nitrates has been the subject of numerous investigations in last century. The nitrite ion, peroxynitrite ion and dioxygen are final products of radiolysis. Radical species have been detected in very low concentrations too.

The assumptions concerning the processes in solid state have been made on the basis of the indirect data obtained after dissolving the irradiated samples. Usually the quantitative determination of decomposition products was performed after dissolving irradiated crystalline nitrates. Nitrite ion was detected by the method of Shinn after dissolving sample in distilled water (pH 7). Peroxynitrite ion was determinated by potentiometric titration after dissolving sample at pH 13. These results were used to build up the mechanism of nitrates radiolysis. The aforesaid methods were shown recently have essential defects [1-3]. Peroxynitrite ion appears to make contribution to measured quantity of nitrite ion [1]. Concentration of peroxynitrite very depends on pH during dissolving of irradiated sample [2, 3]. It is necessary measuring of decomposition products concentrations carry out only in solids to build up correct mechanism of nitrates radiolysis.

The present study therefore aims determination of kinetics of accumulation nitrite and peroxynitrite by optical spectroscopy in solid potassium nitrate.

2. Experimental

The potassium nitrate single crystals were grown by slow evaporation of saturated aqueous solutions. The all experiments were made on polished crystals cut parallel to growth faces of the KNO_3 crystals. The samples were irradiated at room temperature by X-ray (180 kV, 20 mA) with a dose rate ~ 2 Gy/s. Optical spectra were recorded by "SPECORD UV – VIS" spectrophotometer with polarized light. The limit of transmission of used polarizator was ~ 280-300 nm. An analyzing polarized light beam was directed to growth faces KNO_3 crystals with electric vector perpendicular (E⊥C) or parallel (E||C) crystallographic C-axis and threefold axis of nitrate ion.

3. Results and Discussion

The absorption spectra of irradiated single crystal KNO_3 in orientation E||C and E⊥C are shown in Fig. 1 and 2, respectively.

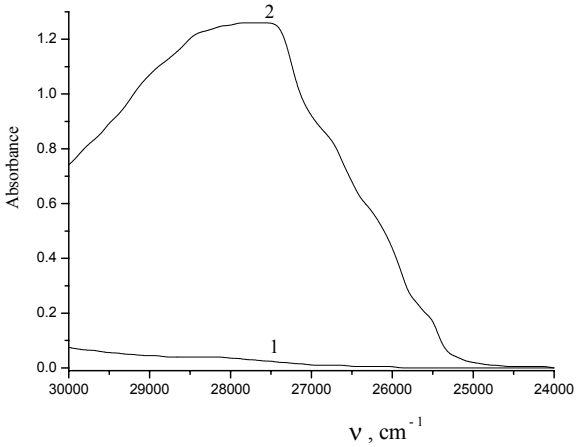

Fig. 1. Optical spectra single crystals KNO_3 (E||C): 1 – unirradiated; 2 – exposed to X-rays by 130 kGy

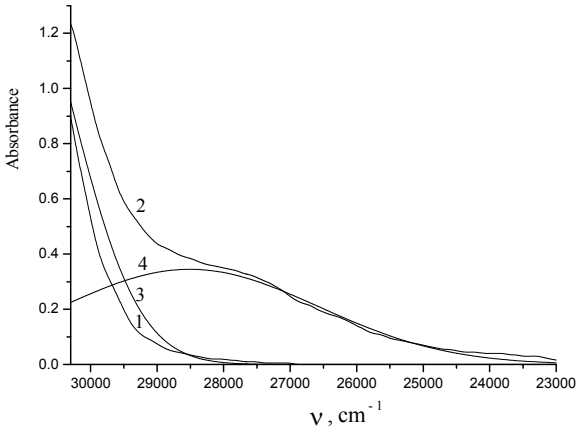

Fig. 2. Optical spectra single crystals KNO_3 (E⊥C): 1 – unirradiated; 2 – exposed to X-rays by 130 kGy; 3, 4 – Gaussian resolution of curve 2

The radiation induced absorption band is centered at 360 nm (E||C) and at 350 nm (E⊥C). The band at 360 nm display vibrational structure ($\Delta\nu \sim 600$ см$^{-1}$).

Optical absorption of peroxynitrite and nitrite ions is well known. The transition of the peroxynitrite at 350 nm is polarized in plane this ion. In crystal KNO_3 it corresponds orientation E⊥C. The transition of the nitrite at 360 nm is polarized normally to plane ion. In crystal KNO_3 it correspond orientation E||C. The

degree of absorption polarization, $e_{\parallel}/e_{\perp}$, of photoinduced peroxynitrite and nitrite ions, introduced by cocrystallization, is equal to 1:10 and 9:1, respectively. Consequently, it can to consider radiation induced absorption is stimulated by nitrite ion in orientation E||C and peroxynitrite ion in orientation E||C.

The kinetics of radiation induced accumulation of optical density at maximums of absorption band of nitrite and peroxynitrite ions is shown in Fig. 3.

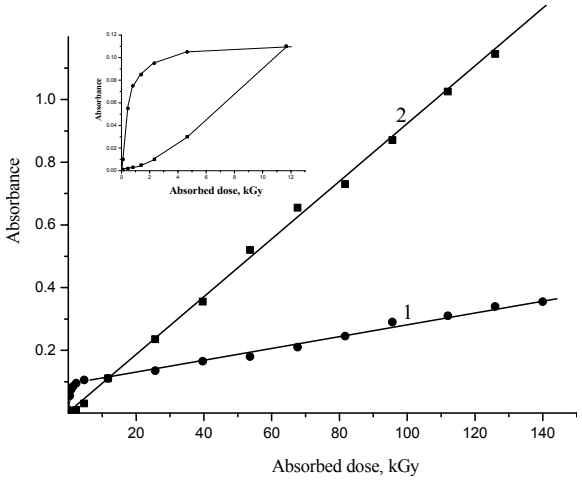

Fig. 3. Dependence of optical absorption single crystals KNO_3 on absorbed dose at: 1 – 350 nm (E⊥C), 2 – 360 nm (E||C). Insertion – initial stage of the dependence

The yield of nitrite as a function of absorbed dose is linear after initial induction stages. In orientation E||C after initial fast accumulation optical density continues to rise linearly at lower speed. The ratio of slopes of linear area of curves is equal 4.4:1.

We consider radiation induced optical absorption in orientation E||C is superposition of absorption of peroxynitrite and nitrite. The difference between degree of absorption polarization 9:1 and 4.4:1 may be accounted by uncomplanar placing nitrite and nitrate ions.

The observed induction period during radiation induced accumulation of nitrite ion show that NO_2^- is secondary product of radiolysis of potassium nitrate.

4. Conclusion

Direct measuring the kinetics of accumulation nitrite ion in single crystal it is shown that NO_2^- is obtaining as a result of secondary processes of radiolysis of potassium nitrate.

References

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