

Paramagnetic Centers In Irradiated $K_{(1-x)}(NH_4)_xClO_4$ Mixed Crystals

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Abstract – The EPR technique were employed to study the nature and measure the concentrations of the paramagnetic centers formed at 77 K and room temperature in $K_{(1-x)}(NH_4)_xClO_4$ ($0 < x < 1$) mixed crystals by ^{60}Co γ - rays. Only the intrinsic defects of the host matrix are observed in all samples. The EPR spectra at lower ammonium content ($0 < x < 0.5$) closely resemble those of pure $KClO_4$. EPR signals from $[ClO_3^-, O^-]$, $[ClO_2, O_2]$ and ClO_3 , ClO_2 and O_3^- are observed in the spectra at 77 K and room temperatures respectively. But at higher ammonium content ($0.5 < x < 1$) the EPR spectra resemble those of pure NH_4ClO_4 and consist of NH_3^+ and ClO_3 lines at both temperatures of irradiation. The initial radiation yields of the principal intrinsic defects are decrease with the impurity ion concentration increasing in the respective host matrix. It is proposed that the observed variations of radiation yields of paramagnetic centers with molar concentration x in γ -irradiated crystals of $K_{(1-x)}(NH_4)_xClO_4$ stem from variations of formation and nature of hydrogen bonds between NH_4^+ and ClO_4^- units of crystal lattice. The correlation between the paramagnetic centers formation and variations of the fundamental internal vibrations spectra of NH_4^+ and ClO_4^- ions is observed and discussed.

1. Introduction

All inorganic perchlorates undergo decomposition when exposed to ^{60}Co γ - rays to form as stable products the chlorine containing anions and molecular oxygen [1–2]. It has been found that γ - irradiation produces the variety of paramagnetic centers [3–5]. The radiation yields of paramagnetic products in crystalline perchlorate matrixes are sufficiently high and comparable with yields of stable end products in most substances. That is why so important to study the nature and accumulation of paramagnetic centers to resolve the perchlorates radiolysis mechanisms problem. One of the ways of the further refinement of this mechanism is to study of not only pure substances but their solid solutions. The preliminary results of the perchlorate solid solutions $K_{(1-x)}(NH_4)_xClO_4$ [6] and $K_{(1-x)}(Tl)_xClO_4$ [7] investigations are recently presented.

The increase of paramagnetic products yields leads to the proportional increase of stable end products [7]. So the stable products formation may be occur via the paramagnetic products.

The goal of the present paper is to study paramagnetic centers accumulation under γ - irradiation of $K_{(1-x)}(NH_4)_xClO_4$ mixed crystals in the whole range of x .

2. Experimental

The $KClO_4$ and the NH_4ClO_4 used were a.r. grade (twice crystallized from redistilled water before use). Mixed crystals of $K_{(1-x)}(NH_4)_xClO_4$ were grown by slow cooling from ~ 370 K to room temperature in thermos of the aqueous solutions of the mixed salts maintaining wide variation of molar concentration x . The average cooling speed was ~ 1.5 K/hour. The sparingly soluble crystals were filtered, twice washed with $KClO_4$ dilute solution to remove the adsorbed impurity from surface layers, and dried in air condition.

Gamma-irradiation of the single crystals of $K_{(1-x)}(NH_4)_xClO_4$ have been made at ~ 77 K (in liquid nitrogen, LNT) or at ~ 310 K (RT). The dose rate ~ 2.5 Gy/s was measured with a Fricke dosimeter system and the dose absorbed by the sample was calculated using the elements mass energy absorption coefficients. The dose values for the solid solutions D_{SS} were calculated as

$$D_{SS} = t [(1-x)D_{KClO_4} + x D_{NH_4ClO_4}] \quad (1)$$

where t – irradiation time, x – means of solution composition, D_{KClO_4} and $D_{NH_4ClO_4}$ are the dose rates of the individual substances.

EPR measurements were made with a RE-1306 X-band spectrometer with 100-kc/sec detection.

The values of initial radiation yields of paramagnetic centres were calculated from initial linear parts of the respective accumulation curve.

3. Results

The ESR spectra of a $K_{(1-x)}(NH_4)_xClO_4$ crystals irradiated with γ -rays at low temperature or ambient temperature consist essentially of the signals from the intrinsic defects of the host matrix. Thus the spectra of samples at $0 < x < 0.5$ obtained at 77 K after irradiation at that temperature represents two abundant defects only: the self-trapped electron in the form of the complex $[O^-, ClO_3^-]$ and the hole defect $[ClO_2, O_2]$. The spectra of samples at $0.5 < x < 1$ represents two abundant defects only too: the hole defect ClO_3 and the secondary electron defect NH_3^+ . Fig. 1 and Fig. 2 shows the variation of relative radiation yields of $[O^-, ClO_3^-]$, $[ClO_2, O_2]$, ClO_3 and NH_3^+ with molar concentration x in γ -irradiated at 77 K crystals of $K_{(1-x)}(NH_4)_xClO_4$.

Elementary processes

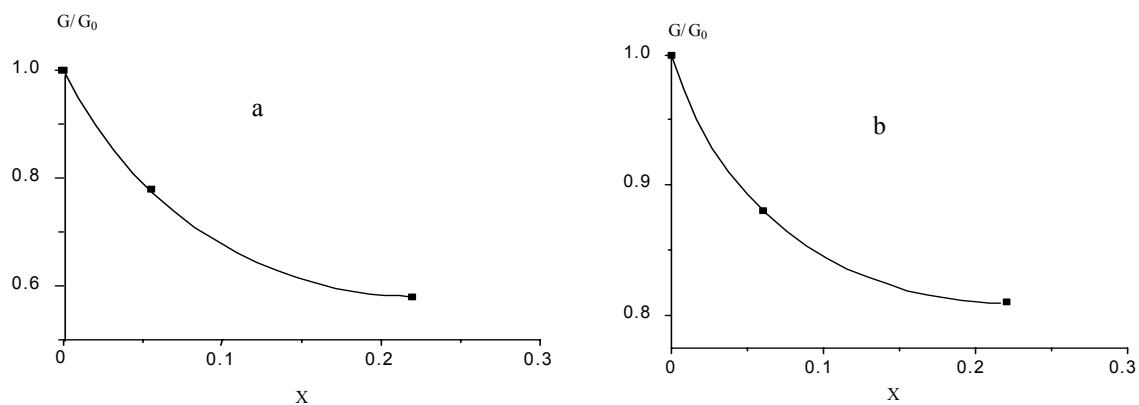


Fig. 1. Variation of relative radiation yields of $[\text{ClO}_3^-, \text{O}^-]$ (a) and $[\text{ClO}_2, \text{O}_2]$ (b) with molar concentration x in γ -irradiated at 77 K crystals of $\text{K}_{(1-x)}\text{NH}_4(x)\text{ClO}_4$. Radiation dose 10kGy. Spectra were recorded at 77 K. G – radiation yield in solid solution, G_0 – radiation yield in pure KClO_4 .

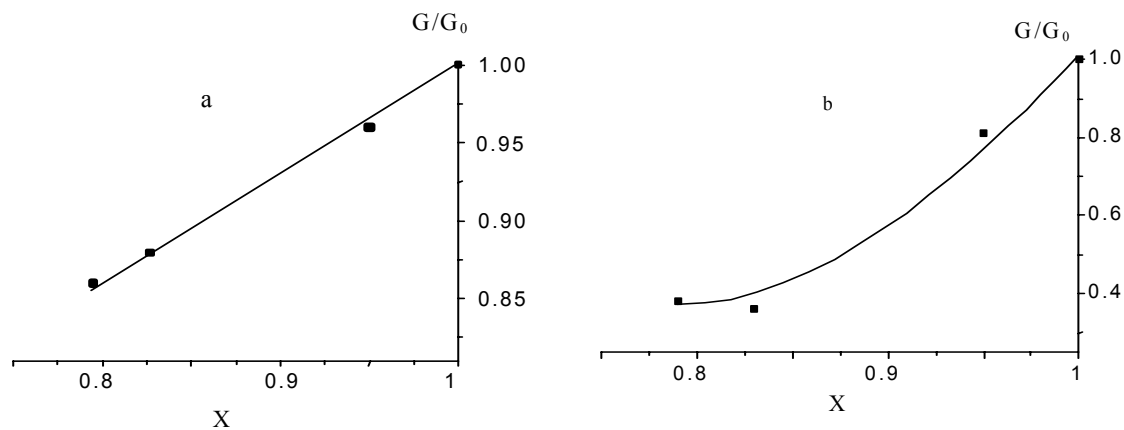


Fig. 2. Variation of relative radiation yields of NH_3^+ (a) and ClO_3 (b) with molar concentration x in γ -irradiated at 77 K crystals of $\text{K}_{(1-x)}\text{NH}_4(x)\text{ClO}_4$. Radiation dose 10 kGy. Spectra were recorded at 77 K. G – radiation yield in solid solution, G_0 – radiation yield in pure NH_4ClO_4 .

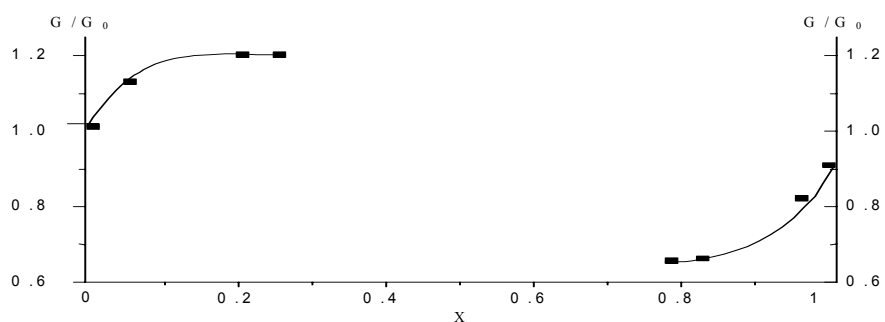


Fig. 3. Variation of relative radiation yields of ClO_3 with molar concentration x in γ -irradiated at 310K crystals of $\text{K}_{(1-x)}\text{NH}_4(x)\text{ClO}_4$. Radiation dose 10 kGy. Spectra were recorded at 295 K. G – radiation yield in solid solution, G_0 – radiation yield in pure KClO_4 .

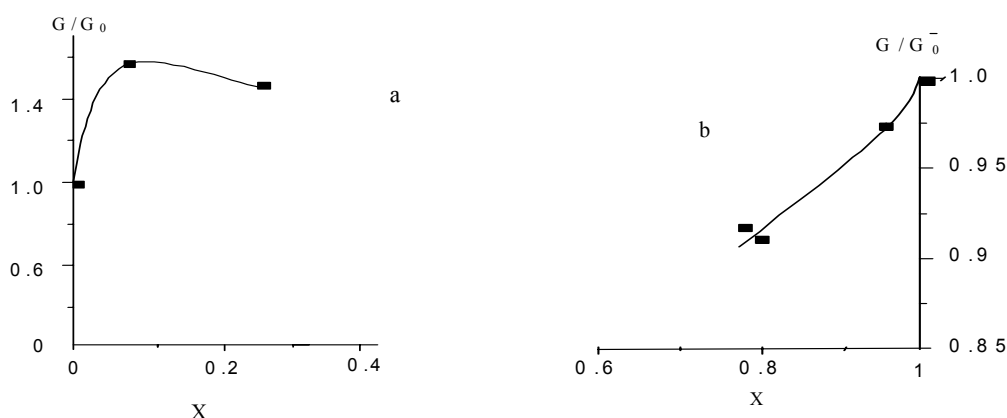


Fig. 4. Variation of relative radiation yields of ClO_2 (a) and NH_3^+ (b) with molar concentration x in γ -irradiated at 310 K crystals of $\text{K}_{(1-x)}\text{NH}_4(x)\text{ClO}_4$. Radiation dose 10 kGy. Spectra were recorded at 295 K. G – radiation yield in solid solution, G_0 – radiation yield in pure KClO_4 (for a) and in pure NH_4ClO_4 (for b).

The curves show that the more the contents of impurity in the host matrix the less the yields of the mentioned intrinsic defects.

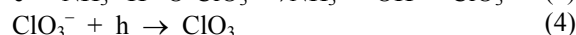
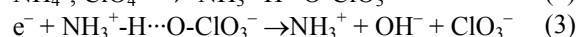
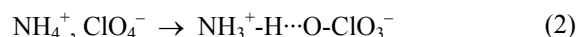
Variation of relative radiation yields of ClO_3 with molar concentration x in γ -irradiated at 310 K crystals of $\text{K}_{(1-x)}\text{NH}_4(x)\text{ClO}_4$ (Fig. 3) has a complex form. Variation of relative radiation yields of ClO_2 and NH_3^+ in γ -irradiated at 310 K crystals has a similar form (Fig. 4). Namely the yields of paramagnetic products at small ammonium content ($x < 0.5$) at first increased but then decreased almost to zero. The ammonium perchlorate intrinsic products radiation yields decreased with the potassium content increasing in the mixed crystals.

4. Discussion

The primary steps in the radiolytic process are assumed to be the ionization and excitation of the perchlorate anion, ClO_4^- . The primary consequence of radiolysis is the breaking of chlorine–oxygen bonds. This anion bonds breaking must be very sensitive to the neighboring cations nature [7].

As it be seen from our previous publication [6], the whole results of cocrystallization curve, crystallographic data and vibrational spectra modes of $\text{K}_{(1-x)}\text{NH}_4(x)\text{ClO}_4$ mixed crystals show that the most of properties variation stem from variations of formation and nature of hydrogen bonds between NH_4^+ and ClO_4^- units of crystal lattice. As the hydrogen bonds formation may completely change the many anion properties, for example the capability for the bonds breaking, the complex form of paramagnetic products variations in the system under consideration may be attributed to the hydrogen bonds nature at different x values. There are the four hydrogen bonds of each ammonia cations with the neighboring anions and vice versa. The presence of K^+ ions in place of NH_4^+ ions

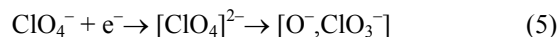
induces to the fourth matrix anions modifications. Therefore it seems to be not unusual the fourfold decreasing of the ClO_3 yield together with the NH_3^+ yield decreasing both in low and ambient temperature (see Figs. 2, 3 and 4). The same reactions



account for the NH_3^+ and ClO_3 formation in the NH_4ClO_4 pure matrix under irradiation and their correlated decreasing in $\text{K}_{(1-x)}\text{NH}_4(x)\text{ClO}_4$ at $0.5 < x < 1$ range.

The hydrogen bonds absence at $0 < x < 0.5$ range leads to the NH_3^+ absence in this mixed crystals.

The correlated decreasing of $[\text{ClO}_3^-, \text{O}^-]$ and $[\text{ClO}_2, \text{O}_2]$ radiation yields of about 2:1 ratio in $\text{K}_{(1-x)}\text{NH}_4(x)\text{ClO}_4$ at $0 < x < 0.5$ is a sequent of the competition for radiation induced electrons between the reactions 3 and 5:



and strongly suggests in favour of the model of formation for $[\text{ClO}_2, \text{O}_2]$ in two-step process [8]:



These observations strongly indicates too that NH_3^+ is formed only in the presence of "normal" hydrogen bonds and another way may be reaction 8



It may account for the $[\text{O}^-, \text{ClO}_3^-]$ and $[\text{ClO}_2, \text{O}_2]$ formation decreasing as well ClO_3 increasing at low ammonium content.

5. Conclusion

The observed correlation between the paramagnetic centers formation and variations of the fundamental internal vibrations spectra of NH_4^+ and ClO_4^- ions in $\text{K}_{(1-x)}\text{NH}_{4(x)}\text{ClO}_4$ mixed crystals strongly indicates that the hydrogen bonds are the important participant of radiolytic processes in ammonium containing matrixes.

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