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Role of Dopant in Annealing of Chemical Radiation Damage in Potassium Nitrate

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The role of cationic vacancy in the annealing of gamma-irradiated potassium nitrate has been investigated using Ba^{2+} as a dopant. Isothermal annealing data show that the pure potassium nitrate is immune to annealing above and below the temperature of crystal transition (Rhombic $\overset{127^{\circ}C}{\rightleftharpoons}$ Trigonal), while the doped crystals undergo recovery by a combination of one first order and one second order process above the phase change and by a second order process below this temperature. The recovery process above 127°C is initially fast (upto 1 hr) but subsequently it slows down to a pseudo-plateau. The proportion of damage which recombines by first and second order processes is 40.6 and 59.4 respectively.

Several workers[1-7] have found that annealing processes are accelerated in crystals in which additives create cationic vacancies, facilitating the movement of radiolytic products. Cationic impurity generates defects and the increase in defect density accounts[8,9] for the greater susceptibility of doped crystals to thermal annealing. In contrast anion doping reduces the sensitivity to recovery[10]. It is, thus, implied that holes trapped at cation vacancies during irradiation are effective in changing the annealing behaviour whereas electrons trapped at anion vacancies interfere with the process. Moreover, the pattern and magnitude of annealing are same at temperatures much above the crystal transition[9,11,12]. The present study relates to the effect of additive (Ba^{2+}) in the annealing of gamma-irradiated potassium nitrate where recovery of damage species induced by electron bombardment has already been studied[11]. Barium nitrate has been used as a dopant because of its greater homogeneity and thermal stability.

Crystals of potassium nitrate (AR, BDH), were doped homogeneously[1] with barium nitrate (AR, BDH), to 1.0 mol per cent by fusing mixtures of these salts in calculated amount at a temperature of 340°C. The mixed crystals were cooled in a desiccator, crushed in an agate mortar and dried at 110°C for 10 hr.

Irradiation was carried out in glass ampoules at room temperature with cobalt-60 γ-rays to a dose of 6.0×10^{-1} MGy at a dose rate of 0.102×10^{-2} MGy hr^{-1}. The damage nitrite was estimated spectrophotometrically at 540 nm according to the procedure of Shinn[13] as modified by Kershaw and Chamberlin[14]. Isothermal annealing studies were carried out at different temperatures between 120 and 160°C in an oil-bath thermostatically regulated to within ± 0.1°C of the required temperature.

The colours of the pure and doped crystals were not affected by irradiation and on dissolving the irradiated salts in water evolution of oxygen took place. Potassium nitrate doped with Ba^{2+} is less susceptible to radiation decomposition than the pure salt, the initial damages being 63.27 and 66.49 μmol NO_2^- g^{-1}, respectively. The lower initial damage in the doped crystals may be due to (i) competition between impurity ion (Ba^{2+}) and radiolysis products for the electrons involved in the radiation chemical processes[15] and (ii) the divalent barium present as a cation impurity perturbs anion(s) on adjacent site(s), thereby establishing conditions for preferential localization of excitons or charge at those anions[16]. Nitrate ions undergoing radiation decomposition at sites adjacent to a Ba^{2+} cation experience, in part, the cation-anion interaction present in barium nitrate. Preferential localization of radiation energy at anions adjacent to Ba^{2+} impurities would therefore decrease the rate of radiolysis of doped crystals relative to pure substance. The data show that pure potassium nitrate is immune to annealing (Fig. 1) below the transition temperature whereas above the transition temperature there is an abrupt recovery of a fraction of the damage followed by a slow change. Usual annealing pattern is found in mixed crystals below 127°C but above this temperature an abrupt recovery of the damage followed by a pseudo-plateau region is observable. The effect of impurity is especially noticeable during the intial periods of recovery. Lattice mobility during the

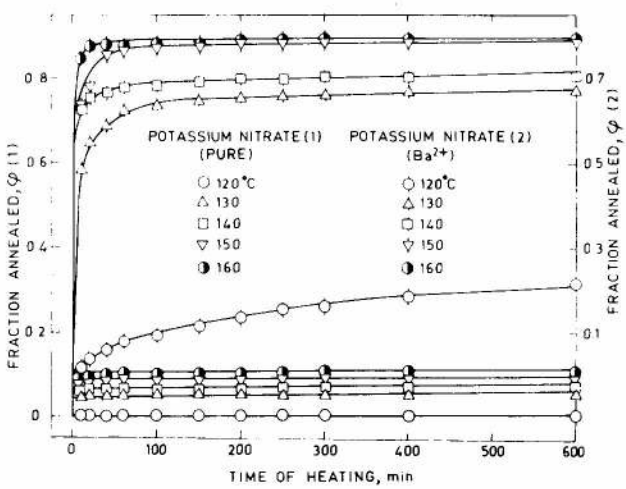

Fig. 1—Annealing of nitrite in gamma-irradiated pure and doped (Ba^{2+}) potassium nitrate.

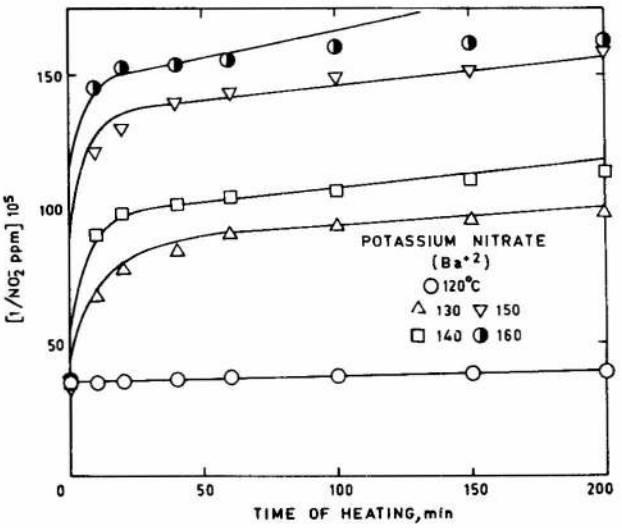

Fig. 2—Second order plot for annealing of nitrite in gamma-irradiated doped (Ba^{2+}) potassium nitrate.

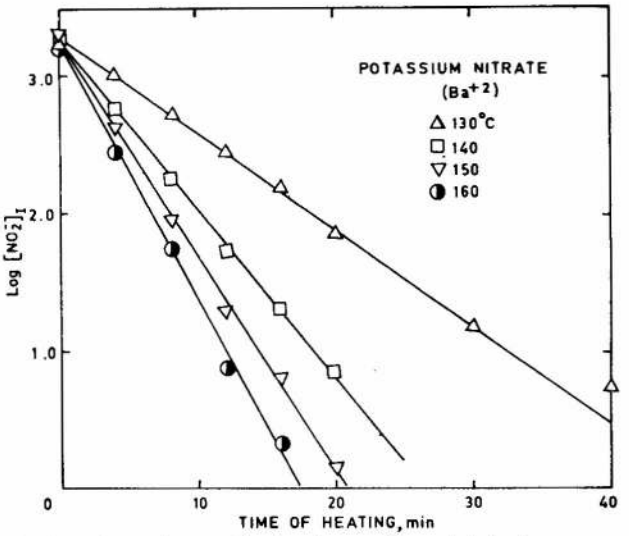

Fig. 3—First order contribution in annealing of nitrite in gamma-irradiated doped (Ba^{2+}) potassium nitrate.

phase change liberates the damage fragments, a proportion of which then rapidly recombines to give nitrate ions[9,11,12]. As the phase transformation leads to loss of most of the damage oxygen from the crystals very little further annealing occurs. Annealing data at 150 and 160°C suggest the same. The fractions (φ) annealed in pure and doped crystals at 150°C and 10 hr of heating are 0.1 and 0.79 respectively. This immunity of the pure compound to thermal recovery can be attributed to small free space in the crystal lattice.

Incorporation of Ba^{2+} in the crystal lattice of potassium nitrate generates cationic vacancies, shallow electron traps due to nitrate radicals tied to such vacancies and increase in the free space in a crystal, which produce appreciable thermal recovery of the damage by facilitating the migration of the mobile fragments[9,17,18].

No significant informations are obtained for the kinetics of the recovery process in pure potassium nitrate due to very low value of φ. But considering the annealing data in γ-irradiated doped crystals from the view-point of conventional chemical kinetics (Figs 2 and 3), it is found that recovery above the temperature of phase change is a combination of one first order (40.6%) and one second order (59.4%) process with activation energies of 53.6 and 76.6 kJ mol^{-1} respectively (Fig. 4). But below the transition temperature the process is purely second order in nature. The first order mechanism in doped potassium nitrate accompanying the phase transformation might well be explained as arising from the liberation of atomic oxygen 'O' followed by the rapid reaction (1),

$$NO_2^- + O \rightarrow NO_3^- \quad \ldots (1)$$

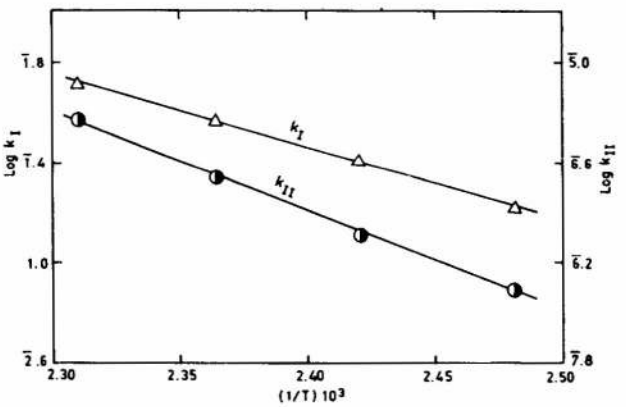

Fig. 4—Energetics of first and second order processes of nitrite in gamma-irradiated doped (Ba^{2+}) potassium nitrate.

while the more plausible second order process is the reaction of NO_2^- and O_2 (Eq. 2) formed in commensurate amounts during radiolysis

$$2NO_2^- + O_2 \rightarrow 2NO_3^- \quad \ldots (2)$$

The probable mechanism for the second order process occurring below the crystal transformation is the same as given in Eq. (2).

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