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ТЕМПЕРАТУРНАЯ ЗАВИСИМОСТЬ ОБРАЗОВАНИЯ И ОТЖИГА РАДИАЦИОННЫХ КОЛЛОИДАЛЬНЫХ ЦЕНТРОВ ОКРАСКИ В ЩЕЛОЧНОГАЛОИДНЫХ КРИСТАЛЛАХ

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TEMPERATURE DEPENDENCE OF RADIATION COLLOIDAL COLOUR CENTRE PRODUCTION AND ANNEALING IN ALKALI HALIDE CRYSTALS

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A b s t r a c t

The investigation results on temperature dependences of production and annealing of radiation colloidal colour centres have been reviewed in this paper. In order to produce such centres in NaCl, KCl and KBr crystals the doses of 10^2-10^4 Mrad as well as irradiation temperatures of 300-600 K and post-irradiation heating of up to 800 K were applied. It has been demonstrated that to form X-centres, it is necessary to have optimal temperature and initial critical dose during both irradiation and post-irradiation heating of crystals. It has been also found that during annealing hole centres formed are different with regard to thermal stability. The possible recombination mechanisms of hole and electron products of radiolysis at post-irradiation heating has been analysed.

1. I N T R O D U C T I O N

Colloidal colour centres serve to indicate the beginning of full damage of a crystal as a result of radiolysis. The study of the production of radiation colloidal centres allows to make some conclusions concerning their nature. Besides, such investigations might lead to a more precise insight into the mechanisms of primary products of radiolysis associated with basic point defects.

Our aim is not to go into detail concerning the production of colloids, since this should be done in special review papers. Thus, a number of interesting review papers on the production of colloidals in ionic crystals have appeared lately [1 - 3]. The above information together with earlier works (for instance, [4,5]), forms good review literature. Unfortunately, the review [5] has not been sufficiently widespread for it has not been even referred to in a later review paper [1].

The present paper deals mainly with our investigation results of temperature dependences of radiation production of colloids in alkali halides during both irradiation and post-irradiation thermal annealing. However, the above investigations have one distinguishing feature, namely, the application of wide temperature ranges (higher than room temperature) and relatively large irradiation doses.

2. E X P E R I M E N T A L P R O C E D U R E

One of the aims of investigation series was to find the relationship of

the formation of simple colour centres (F, V, etc.) and colloidal colour centres. Hence, the basic investigation method used was the absorption spectra measuring within the range of 200-1000 nm. A single type of colloidal centres - X colour centres - can be well identified by absorption spectra of alkali halides. It is known [5] that X-centres are not identical to colloidal particles of a metal but might possibly be the aggregates of many F-centres. The bulk of the results presented here are associated with X-colour centres.

The irradiation was mainly performed by a linear accelerator of electrons (3.5 MeV, 1 Mrad/s). Some irradiations were also carried out at a nuclear reactor (20 krad/s) [5]. Temperature changes during irradiation were also caused by irradiation heating; and as a result of either additional heating or cooling. The measurement of absorption spectra took place at room temperature just after irradiation or post-irradiation heating.

The basic measurements were done for NaCl and KCl crystals which are classic objects in physics of colour centres in alkali halides. Besides, the effects connected with radiation colloidal production were first observed in common salt NaCl - blue colour of these natural crystals is due to colloidal particles of sodium formed as a result of irradiation caused by radioactivity background [6]. On the contrary to this, natural mineral KCl (silvinite) has no colour which can be explained, as it was shown in [5], by both relatively high temperature and intensity of irradiation. Already in 1957 Compton applied NaCl crystal for systematic investigations of radiation production of colloidal colour centres [7]. In 1957 Yoshida and Ikeda [8] performed first irradiation of NaCl at high temperatures and showed that colloidal production in NaCl depends on dose rate. It is necessary to point out another advantage of NaCl and KCl applied for investigation. These crystals have a more primitive spectrum (if compared, for instance, with that of LiF), and this allows to analyse the characteristics of radiolysis by optical absorption.

3. COLLOIDAL PRODUCTION DURING IRRADIATION

In early 70-s some doubts arose concerning the effect of radiation colloidal production in other alkali halides beside NaCl. It was found by us [9, 10] that colloidal production in KCl occurs at larger irradiation temperatures than room temperature.

The value of optimal temperature of colloidal production depends on dose rate (Fig.1). This dependence on dose rate (Fig.1) is associated with the production of halogen products of radiolysis and will be discussed further. In general, the dependence of yield of colloidal centres of irradiation temperature can be shown by a curve with a well pronounced maximum. Such dependence was obtained also for NaCl [11,12] (Fig.2).

The second condition of colloidal production during irradiation is the necessary presence of critical primary dose to initiate the process (Fig.3). The above peculiarity is expressed better for KCl crystal [5,9] than synthetic NaCl. At high irradiation temperature (160°C, Fig.3) KCl crystal remains transparent (the production of significant amount of F-centres is absent) until the predetermined critical dose is reached. X- and F-centres appear later. The number of F-centres grows slowly, and their presence in absorp-

tion spectrum of crystal is defined by thermodynamic equilibrium with X-centres which is the same as in the case of additively coloured crystals.

The similar critical primary dose of colloidal production can be also observed for natural NaCl crystal. As known, Compton [7] did not find the production of X-band of natural NaCl even after irradiation at room temperature by a dose of 10^9 r though a well expressed X-band is observed for synthetic NaCl after it is irradiated by the dose of $2 \cdot 10^8$r. We found in our investigations [11] that for the initiating of the production of the pronounced X-band in NaCl, there must be the dose of ~1000 Mrad and high temperature. Under similar irradiation conditions the optimal temperature of production of colloids for natural NaCl (160°C) is by 50°C higher than that for synthetic NaCl (Fig.2).

The investigation of radiation production of impurity colloidal sites Ag and Tl [9] allowed to conclude the following [5]. During the first stage of irradiation impurity colloidal sites are formed (approximately at the doses of 50 to 500-1000 Mrad) while colloidal centres of alkali metal (at the doses exceeding 200-1000 Mrad) are produced later during the next stages of irradiation.

Close to the production of colloidal centres of metal there is analogous process when large aggregates of interstitial halogen centres are formed. Optical absorption investigation of the latter process is rather difficult since the bands of these centres are weakly expressed in absorption spectrum.

It has been found in our studies [13] that the location of maximum of absorption band for NaCl are shifted towards short waves from 225 to 205 nm when the electron irradiation dose is increased from 10^2 to 10^4 Mrad. The same shift of V-band maximum is also reported if the irradiation temperature is changed, the doses being constant.

We assume that V-band of absorption can be expressed in terms of superposition of basic bands defined by the absorption of both V-centres and its aggregates of various size. The shift of V-band towards short waves with the increase of either the dose or irradiation temperature shows that growing contribution to the absorption spectrum is mainly due to the aggregates of V-centres with larger dimensions, i.e. radiolysis can be shown schematically as

$$F \rightarrow X \rightarrow \text{metal} \qquad (1)$$

$$V_2 \rightarrow V_3 \rightarrow (V_2)_n \rightarrow \text{halogen} \qquad (2)$$

The above scheme assumes also the analogy of vacancy and interstitial centre coagulation, as well as analogous manifestation of these processes in absorption spectra (the shift of the bands occurs due to the increase of aggregate centre dimensions). In X-centre there is a phase transfer to metal while in large aggregates of V_2-centres it results in gaseous halogen.

In order to explain radiolysis it is crucially important to understand the interaction of electrons (F, F_n, X) with hole ($H, V_2, (V_2)_n$) centres. The processes going on during the irradiation, as well as post-irradiation heating, can be explained basing upon an assumption of non-uniform distribution and spatial separation of electron centre clusters on one hand, and hole centres, on the other hand. Their transformation and coagulation take place within the above centre clusters.

The aggregates of V_2-centres are likely to arise in the region of dislocation loops [12] with a high local concentration of V_2-centres. The overlapping of regions with clusters of interstitial halogen atoms and radiation defects in cation sub-lattice (of V_F-centres) might also lead to the production of V_2-centre clusters.

In accordance with the paper by Hobbs [12], the dislocation loops act as efficient traps of H-centres. But this can lead to the situation when high intensity of irradiation may stimulate the spatial separation of primary radiation defects with a resulting production of corresponding aggregates.

4. COLLOIDAL PRODUCTION DURING POST-IRRADIATION HEATING

The irradiated crystal, if considered only in terms of electron colour centres, could be compared with additively coloured crystal. The degree of this comparison might be relatively expressed by efficiency of F→X transformation g [14,16]. The part of primary F centres which has been transferred to X centres as a result of coagulation of F centres (taking into account that areas under F and X bands remain constant during transformations in an additively coloured crystal [15]) is assumed to be the measure of the above efficiency,

$$g = \frac{H_X \cdot \alpha_X}{H_F \cdot \alpha_F} , \qquad (3)$$

where H_X, H_F - half-width of X- and F-bands, respectively, α_X, α_F - absorption factors of X-band during optimal temperature of annealing, and F-bands before heating, respectively.

The following values of g for crystals irradiated by the dose of 10^4 Mrad at 60°C have been obtained:

	NaCl	KCl	KBr
During heating in the dark	0.78	0.26	0.14
When lighted at 6000 lx	0.87	0.45	0.38

As seen from the above data, transformation efficiency F→X is much larger during heating and additional illumination if compared with heating in the dark. The same analogy, as known [15], is observed also for additively coloured centres. The value g allows to evaluate roughly the amount of electron products of radiolysis in clusters but not in single centres. Of course, a part of F centres forming clusters cannot coagulate to produce colloidal centres - they recombine with hole centres.

We observed the production of X centres for three crystals - NaCl [11], KCl and KBr [16] as a result F→X transformation. The minimum doses providing the transformation F→X for these crystals when irradiated at 60°C are as follows (in Mrad):

$$NaCl - 5 \cdot 10^2, \quad KCl - 5 \cdot 10^3, \quad KBr - 10^4$$

It should be noted, however, that for KBr crystal we did not observe the production of X-centres during the process of irradiation but only during post-

irradiation heating.

While heating the irradiated crystals, a number of bands were found in short-wave region of absorption spectrum, and their distance was anticipated by the calculations basing on Mi formulae [17]. The above bands have the corresponding maximum (nm), for

NaCl - 310, KCl - 380, KBr - 410.

5. THERMAL ANNEALING OF IRRADIATED CRYSTALS

All crystals irradiated by the doses of 10^2-10^4 Mrad at temperatures above room have the following transformation and annealing of colour centres. At the beginning, there is a decrease of F band intensity accompanied by a slight growth of M-band and a significant growth of X-band. A sharp decrease of X-band correlates with a rather insignificant change of V-band. On the contrary, V charge starts changing sharply at high heating temperatures only when the final annealing of X-centres occur. A slight shift of V-band towards shorter wavelength is also reported, i.e. it might be shown by the scheme: $V_2 \rightarrow V_3 \rightarrow (V_2)_n$. For NaCl a gradual shift of X-band towards greater wavelength is observed during heating, which could mean an increase of particle size as anticipated by the equations of Mi.

The growth of irradiation temperature leads to the change of typical annealing temperatures. For instance, when increasing irradiation temperature by 100°, from 60° to 160°C, at one and the same dose of 10^4 Mrad, of X and V centre annealing temperature increases too. For NaCl this increase was 50°C for KCl 20°, KBr 15°, respectively. There is analogous growth of annealing temperature if the irradiation dose is increased. For instance, for NaCl crystal irradiated at 200°C by the doses of 10^3 and $2.5 \cdot 10^4$ Mrad, the annealing temperature has increased by 80°C.

Our experiments [18] have shown that the annealing of NaCl crystals irradiated at 200°C by the dose of $2.5 \cdot 10^4$ Mrad is a two-stage process (Fig.4). In these experiments optical absorption spectra, concentration of metal atoms in large particles by the electron microscopic data as well as mechanical density was measured. The annealing of the majority of V centres (70 %) in the first stage is accompanied by a full annealing of X band and a partial increase of mechanical density. The number of V centres annealed and the value of mechanical density change are approximately the same. During the second stage V centres are completely annealed, the mechanical density regained, and there is a considerable decrease of concentration of sodium atoms in colloidal particles. Thus, during both the stages of annealing interstitial helogen recombines with X centres and the atoms of colloidal metal, respectively, which leads to the increase of density.

The two-stage NaCl annealing presented in this paper is reported to occur only if the irradiation temperatures exceed 100-130°C. For instance, if NaCl crystals are irradiated at 60°C, there is only a single-stage annealing. The temperature of 130°C (400 K) is taken as a characteristic temperature T_a, i.e. the border line between these two variants of annealing and, consequently, between the two variants of radiolysis products created during irradiation.

The above experimental results allow to analyse the possible mechanisms of thermal decay of X centres and aggregates of V_2 centres (Fig.5). The first possibility: F centres are splitted up from X centres and, while migrating in crystal, recombine with the aggregates of V_2 centres. The second possibility: halogen atoms split up from aggregates and, while migrating in crystal, recombine with X centres. The models, irradiation and annealing conditions, relaxation equations are presented in Figure 5.

For stationary conditions of annealing the system of equations is applied in the form of the kinetic equation of thermal damage (decay) of X centres and can be expressed as [19]

$$\frac{dn'_F}{dt} = f(n'_F)\, e^{-E/kT}, \qquad (4)$$

where f(n'F) is a continuous function while E is the sum of binding and migration energy of F centre.

The activation energy of the thermal damage of X centres in irradiated crystals was calculated [19] basing on these assumptions and experimental data:

NaCl	(10^3 Mrad, 330 K)	1.04 ± 0.05 eV
	(10^3 Mrad, 475 K)	1.65 ± 0.09
KCl	(10^4 Mrad, 330 K)	1.01 ± 0.06
	(10^4 Mrad, 435 K)	1.43 ± 0.08

In additively coloured crystals this energy has the following values

NaCl - 1.61 ± 0.07 eV; KCl - 1.50 ± 0.09 eV.

In other words, thermal damage of F centres in crystals irradiated at larger temperatures is similar to the process in additively coloured crystals.

Thus, during post-irradiation heating of crystals after they have been irradiated at large doses of low-temperature irradiations (up to 400 K), there is mainly thermal damage of aggregates of V centres into mobile constituents which further recombine with immobile X centres. On the contrary, after high-temperature irradiation (more than 400 K) there is thermal conversion of X centres into F centres, the latter will later damage the immobile aggregates of V_2 centres.

The increase of thermal stability of complex colour centres due to the growth of both dose and irradiation temperature can be explained by the increase of binding energy in large metal and halogen centres.

The necessary condition for the production of X centres by heating is a high primary cencentration of F centres which must be larger than the concentration at thermodynamic equilibrium: n_{F0} $n_F(p)$ (Fig.5). In the first stage of annealing the sedimentation of F centres on the surface of X centres prevails over both a reverse process of F centre evaporation from this surface and recombination processes. As the annealing temperature increases (second stage), the splitting of F centres from the surface of X centres is going to prevail over their sedimentation and simultaneously recombination into mobile constituents becomes more pronounced due to thermal damage of V_2 centre aggregates ($T_{irrad} < T_a$) or X centres ($T_{irrad} > T_a$). The process of transformation and recombination of colour centres can be described by a set of kinetic equations for each case (Fig.5). There was a good aggreement between calculation and experimental curves of temperature dependence.

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Fig.1

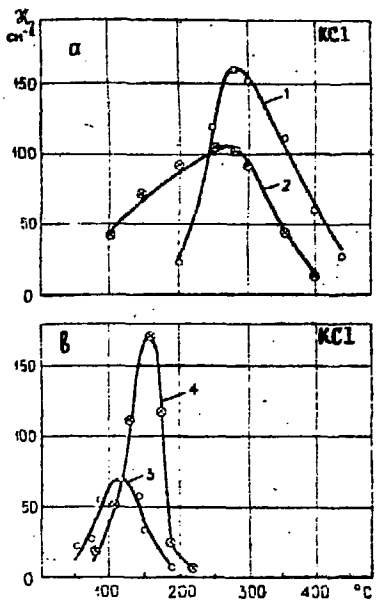


Fig. 1. Temperature dependence of X centre production in KCl crystals [5,10].
a - additively coloured crystal. Heating: 1 - in the dark, 2 - under light;
b - during irradiation in a nuclear reactor (5.5h). Dose rate: 3 - 7.5 rad/s , 4 - 17 krad/s.

Fig.2

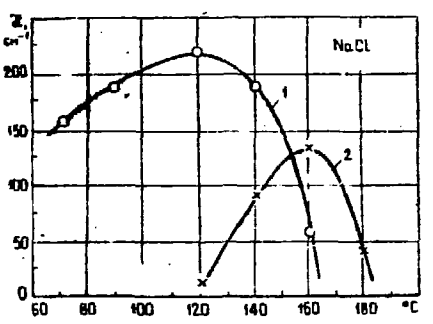


Fig. 2. Temperature dependence of X centre production in NaCl crystals [5,11]. Absorbed dose at each irradiation - 480 Mrad.
1 - synthetic crystal,
2 - natural crystal.

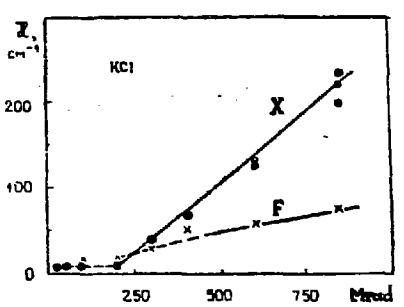


Fig. 3. Dose dependence of the production of F and X colour centres in KCl crystals [5,9]. Irradiation temperature 160°C. Dose rate - 13 krad/s.

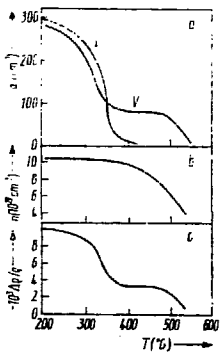


Fig. 4.

Post-irradiation heating temperature dependences of various characteristics of NaCl crystal irradiated at 200°C by the dose of $2.5 \cdot 10^4$ Mrad [18].

a - coefficients of V and X absorption bands;

b - the concentration of a colloidal metal atoms;

c - relative change of mechanical density.

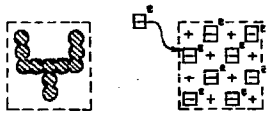
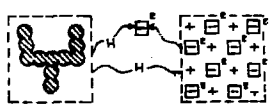
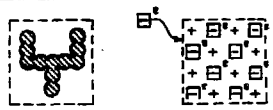
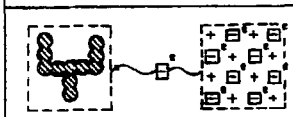
$(V_2)_n$ centre	X centre	irradiation and annealing conditions	corresponding equations
		$T_{irr} < T_a \approx 400K$ $n_{F0} > n_F^{(p)}$ I stage of annealing $F \longrightarrow X$	$\frac{dn_F}{dt} = 4\pi D_F r_X n_X n_F^{(p)} - 4\pi D_F r_X n_X n_F - 4\pi D_H r_0 n_H n_F$
		$n_F < n_F^{(p)}$ II stage of annealing $(V_2)_n \rightarrow 2nH + X \rightarrow 0$	$\frac{dn'_F}{dt} = 4\pi D_F r_X n_X n_F - 4\pi D_F r_X n_X n_F^{(p)} - 4\pi D_H r_X n_X n_H$
		$T_{irr} > T_a \approx 400K$ $n_{F0} > n_F^{(p)}$ I stage of annealing $F \longrightarrow X$	$\frac{dn_F}{dt} = 4\pi D_F r_X n_X n_F^{(p)} - 4\pi D_F r_X n_X n_F - 4\pi D_F r_V n_V n_F$
		$n_F < n_F^{(p)}$ II stage of annealing $X \rightarrow 2nF + (V_2)_n \rightarrow 0$	$\frac{dn'_F}{dt} = 4\pi D_F r_X n_X n_F - 4\pi D_F r_X n_X n_F^{(p)}$

Fig. 5. The scheme of transformation and annealing of colour centres during post-irradiation heating.

n_F - the concentration of F centres migrating in crystal, the change of this concentration being defined by thermal damage of X centres and annihilation with hole aggregates;

D_F - diffusion factor of F centres, r_X and r_V - radii of X centres aggregates of V_2 centres; n_X and n_V - the concentrations of these X centres and aggregates of V_2 centres;

$n_F^{(p)}$ - the concentration of free F-centres at thermodynamic equilibrium,

n'_F and n'_H, - the concentration of F centres and halogen atoms constituating X centres and aggregates of V_2 centres;

D_H - diffusion factor of interstitial atom of halogen,

n_H - the concentration of halogen atoms migrating in crystal,

r_o - the distance between the centres of neighbouring anion vacancies.