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X-RAY COLORATION OF SODIUM CHLORIDE CRYSTALS CONTAINING SODIUM COLLOID PARTICLES

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Abstract: The effect of X-ray irradiation on single crystals of sodium chloride containing sodium in stoichiometric excess in t he form of colloid particles was investigated by measuring optical absorption spectra.

No influence of X-rays on colloid particles was found. The concentration of F-centres created during the first stage of irradiation was about 2.5 times higher than in pure crystals irradiated with the same dose and was independent of the way in which the colloid particles had been formed.

1. Introduction

F-centres in additively coloured alkali halide crystals may coagulate into colloid particles if the excess of alkali metal is above the equilibrium concentration of F-centres[1]. Siedentopf[2] already knew that mild heating of additively coloured and quenched NaCl crystals causes coagulation of F-centres into colloid particles and that at higher temperature the colloids disperse again into F-centres. The growth of colloid metal by heating is accelerated by illumination[3, 4]. Obviously, the ionization of F-centres assists in the formation of colloids. Doyle[5] assumes that colloid particles become negatively charged by trapping electrons under illumination and promote their own growth by attracting negative ion vacancies. Tsal *et al.*[6, 7] also observed that anion vacancies played an important role in the coagulation of F-centres.

The initial stage of coagulation of F-centres and the structure of colloid nuclei are not yet known. In a crystal containing colloid metal a great variety of centres of colloid type may be present, giving rise to a characteristic colloid band in the absorption spectrum of the crystal.

NaCl crystals containing colloid particles of sodium are blue in transmitted light. Under X-ray irradiation their colour changes. Visual inspection as well as preliminary measurements of absorption spectra showed that the rate of F-centre formation was higher in blue than in colourless samples. The purpose of this work was to investigate by optical absorption spectra whether colloid centres played a role in this phenomenon.

2. *Experimental procedure*

Single crystals of sodium chloride purchased from the Harshaw Chemical Co. were used in our experiments. Sodium colloid particles were obtained by introducing *F*-centres at high temperature and by cooling crystals to room temperature. Two techniques of introducing *F*-centres were used. Additive coloration was carried out in potassium vapour at a temperature of 650° C in Supremax glass tubes. After cooling to room temperature crystals became blue. The other technique was the electrolysis of the crystal at 650° C using a pointed cathode, until a nearly uniform coloration was attained. If the crystals were rapidly removed from the furnace and air cooled they became violet-blue, while they became blue if they were cooled in the furnace.

The coloured samples were cleaved into thin plates about 0.8 mm thick and irradiated with *X*-rays from a Hilger fine focus tube with a copper anode operated at 39 kV and 3 mA. The distance from the crystal to the focus was 7 cm.

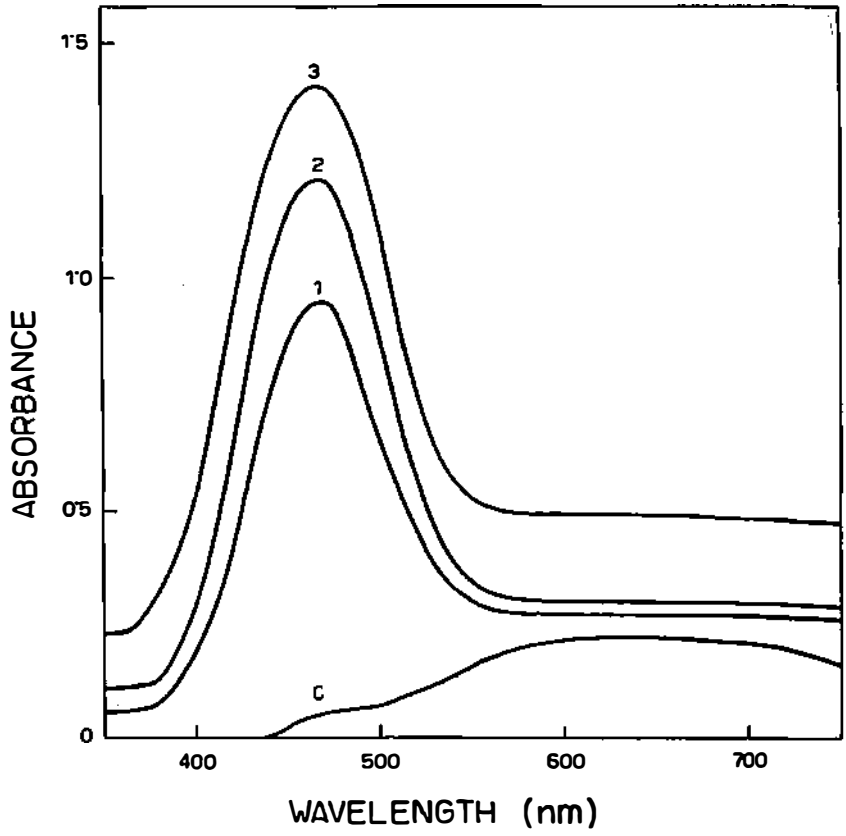

Fig. 1. Absorption spectra of additively coloured NaCl: *0* crystal after additive coloration, *1* after 28, *2* after 55 and *3* after 88 minutes exposure to *X*-rays.

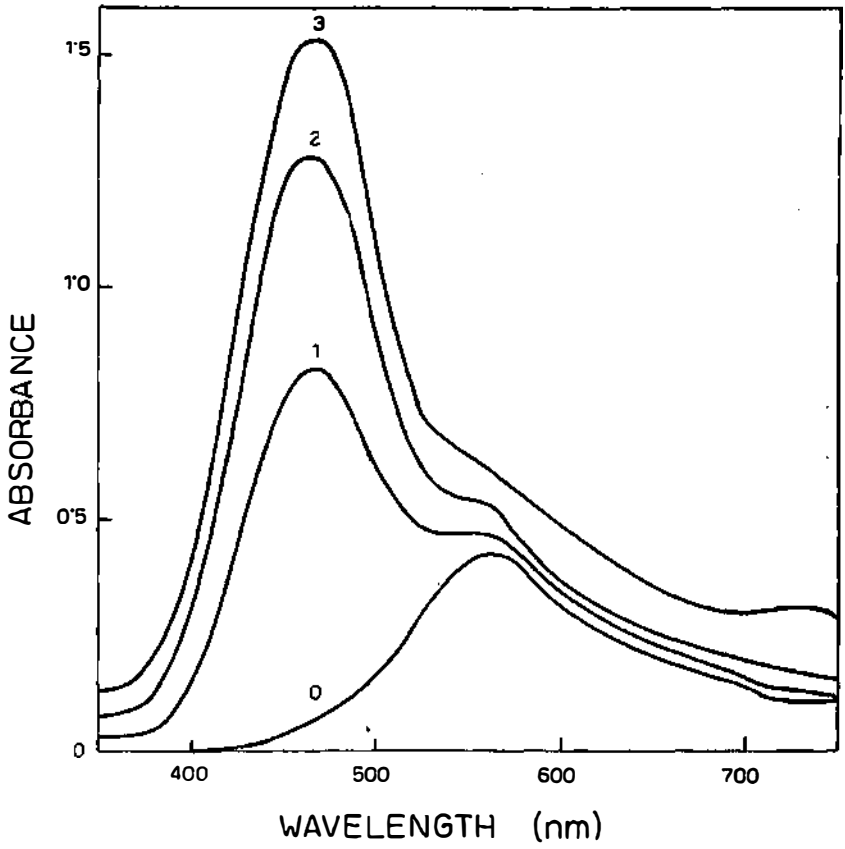

Fig. 2. Absorption spectra of electrolytically coloured and air cooled NaCl: *0* crystal after electrolytical coloration, *1* after 31, *2* after 65 and *3* after 100 minutes exposure to *X*-rays.

Optical absorption measurements were performed with the Perkin-Elmer recording type spectrophotometer Model 137 UV.

Except during absorption measurements the samples were kept in the dark to prevent optical bleaching.

3. Results and discussion

Before introducing *F*-centres from each crystal a part was cleaved off to make possible the comparison of *X*-ray irradiation effects on both blue and colourless crystals.

Optical absorption spectra of blue crystals measured before *X*-ray irradiation show a broad absorption band. In blue crystals, which were additively coloured or electrolytically coloured and furnace cooled, the maximum is not well pronounced, while in violet-blue samples, which were electrolytically

coloured and air cooled, the absorption maximum is at about 570 nm, as shown in Figs. 1 and 2 by curves *0*, respectively. Comparing these extinction curves with the curves calculated by Savostianowa[8] the mean size of colloid particles could be estimated. In blue crystals, additively or electrically coloured, particle diameters between 40 and 80 nm are obtained, while in the rapidly cooled violet-blue samples smaller diameters of approximately 25 nm are obtained.

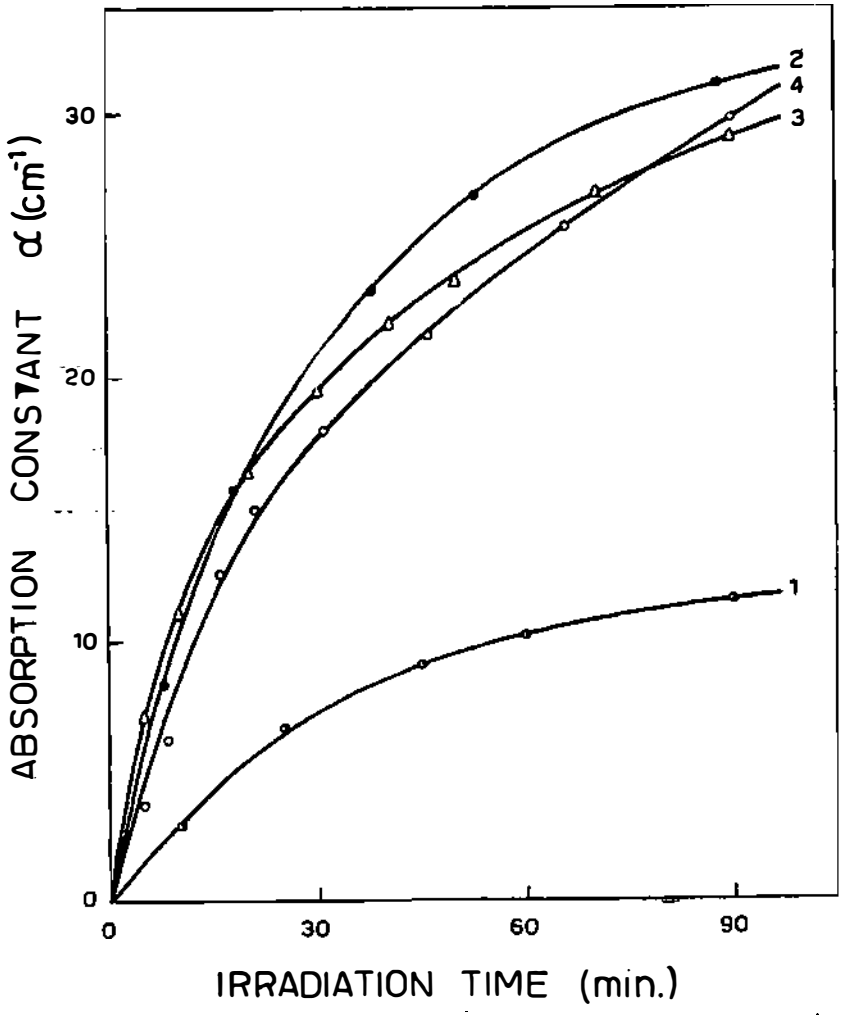

Fig. 3. Growth of the F-band as a function of irradiation time. Curve *1* colourless NaCl specimen, *2* additively coloured, *3* electrolytically coloured (furnace cooled), *4* electrolytically coloured (air cooled).

The extinction curves of the irradiated blue crystals taken after various times of irradiation show that the change of colour is due to the appearance

of the F-band as seen in Figs. 1 and 2. From the curves the absorption constant α for the wavelength of the F-band maximum is determined. In Fig. 3 the absorption constant α is represented as a function of the irradiation time τ. Curve *1* corresponds to the initially colourless crystal, curve *2* to the additively coloured crystal whose extinction curves are given in Fig. 1. Curves *3* and *4* correspond to the slowly and rapidly cooled electrolytically coloured crystal, respectively. The extinction curves belonging to the rapidly cooled crystal are shown in Fig. 2.

Table

Experimental data of the number of F-centres in cm^3 created during various irradiation times

Sample	*1*	*2*	*3*	*4*	τ (min)
$N \cdot 10^{-17}$	0.39	1.06	1.01	0.92	30
	0.54	1.44	1.32	1.27	60
	0.61	1.63	1.51	1.53	90
K	1	2.72	2.60	2.36	30
	1	2.67	2.46	2.37	60
	1	2.67	2.47	2.51	90
K_{mean}	1	2.68	2.51	2.41	

From the absorption constant α and the measured F-band half-width the average concentration N of F-centres was calculated for various times of irradiation τ using Smakula's formula[9]. The results are given in the Table. The number denoting the sample corresponds to the number of the curve in Fig. 3. K is the ratio between the concentration of the F-centres generated in blue crystals and those in colourless crystals for the same dose of irradiation. The results are in good agreement with the results obtained by investigating other crystals of the same kind.

The curves obtained by subtracting graphically the F-band from the total extinction curves were compared. Blue crystals showed the same behaviour independent of the way in which they had been coloured. The shape of the colloid band was not affected by X-ray irradiation, except for small changes

in the tails of the bands. Hence the conclusion may be drawn that the colloid particles do not disintegrate during irradiation times applied and thus they do not assist in the F-centre formation by their disintegration.

Examining the X-ray coloration of γ-irradiated and thermally partially bleached NaCl crystals, Sastry[10] observed decrease of »C_1«-absorption band which has the characteristic properties of a colloid band with the maximum at 560 nm. As in this case the colloids were created in a different way than in our crystals the same behaviour of the crystals should not be expected. The stability of colloids in our case may be due to the excess of sodium which is present in the crystals before irradiation.

The only effect of X-rays on our crystals, which was measurable in the visible region, is the enhanced formation of F-centres. On the average, the concentration of F-centres is 2.5 times higher than in colourless crystals for the same dose of irradiation. The increased rate of F-centre formation can be explained by the following arguments. As it is known[11, 12, 13, 14] at the first stage of coloration with X- or γ-rays, the F-centres are created from the anion vacancies initially present in the crystal. During the process of colloid formation in blue crystals, the F-centres are annihilated and an excess of anion vacancies in comparison with their number in stoichiometric crystals can be expected. Further, it has been unambiguously proved that the structural defects introduced by the deformation of crystals enhance the rate of F-centre formation under X-ray or γ-ray irradiation[15, 16]. Being of submicroscopic size colloid particles cause distortion of the lattice throughout the volume of the crystal. The effect of this distortion can be observed by comparing X-ray diffraction micrographs, taken by the Berg-Barrett technique of the cleavage surface of blue and colourless crystals.

Thus, the very presence of colloid particles is responsible for the increased rate of F-centre formation.

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DJELOVANJE RENDGENSKIH ZRAKA NA KRISTALE NATRIJEVA KLORIDA S KOLOIDNIM ČESTICAMA NATRIJA

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Sadržaj

Metodom apsorpcijskih spektara u vidljivom području, istraženo je djelovanje rendgenskih zraka na modre kristale natrijeva klorida, koji sadrže stehiometrijski suvišak natrija u obliku koloidnih čestica. Pokazalo se je, da kod iste doze zračenja broj stvorenih F-centara je oko 2.5 puta veći nego u bezbojnim kristalima stehiometrijskog sastava, bez obzira kojom su se metodom koloidne čestice formirale u kristalu. Nisu primijećene nikakve promjene koloidnog sastava. Povećana brzina stvaranja F-centara pripisuje se većem broju anionskih praznina i distorziji rešetke zbog prisutnosti koloidnih čestica.