

# Study of the structure and optical properties of model salt particles of marine aerosol

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The electron microscopy, X-ray crystal analysis, and infrared spectroscopy methods are applied to identification of new compounds in model salt particles exposed to high-energy radiation. Analysis made showed that a plenty of new substances is formed in the system “air – alkali-halide particle” after activation by ultraviolet radiation, X-rays, and gamma rays. It is shown that natural and anthropogenic radiation factors in the atmosphere can cause similar composite transformations of marine aerosol and contribute to chemistry and optics of the atmosphere.

## Introduction

It is known that the atmosphere above the Global Ocean contains great amount of alkali-halide particles that form marine aerosol. The studies performed in recent years showed an interesting reaction yielding generation of nitrate in marine salt particles under the effect of  $\text{NO}_2$ . Junge discovered the highest content of nitrates in the shore zones of the northwestern part of the U.S.A.<sup>1</sup>

It becomes clear from these observations that generation of aerosol nitrate depends on the presence of both sea spray particles and  $\text{NO}_2$ , and the concentration of  $\text{NO}_2$  in some shore zones is increased due to anthropogenic pollution. In some shore zones, the  $\text{NO}_3^-/\text{Cl}$  ratio in giant particles is about 0.5. Based on these results, Robbins et al.<sup>2</sup> have studied this reaction in a lab. In the presence of water,  $\text{NaCl}$  reacts with  $\text{NO}_2$  at room temperature thus generating nitrosylchloride, which very easily leads to hydrolysis or photolysis. For less than 10 min, the bound part of chlorine undergoes transformation, and this part increases with the increase of relative humidity. This part is almost independent of the available concentration as long as the concentration ratio of  $\text{NaCl}$  and  $\text{NO}_2^-$  remains constant. Nitrites in this case are not detected.

Summarizing, we can say that these observations are indicative of the release of  $\text{Cl}$  from marine salt particles. The effect of both chemical and physical factors connected with exposure to high-energy radiation on the mechanism of this process is still unstudied.

Radiation-chemical transformations of alkali-halide crystals were studied in Refs. 3 and 4.

To understand the processes of formation and transformation of marine aerosol, knowledge of its chemical composition is necessary. Usually, this information is obtained from analysis of particles pre-deposited onto a filter or collected on an impactor. This analysis requires high-sensitivity analytical methods to be applied, because the sample mass does not exceed

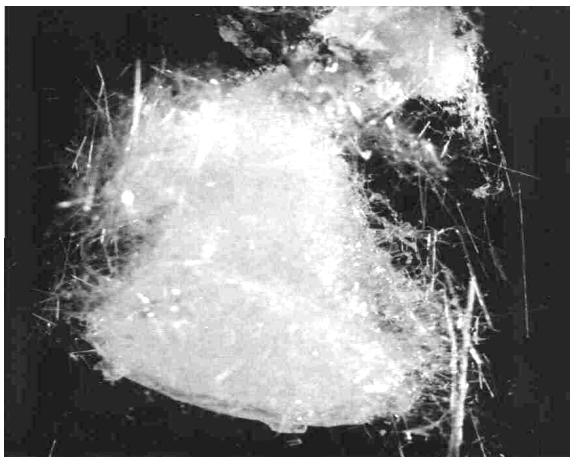
several milligrams. The most widely used methods of analysis give the information on the element or ion composition of a sample. However, the question “In what chemical form were ions and elements in the initial particles” remains open yet. To answer this question is especially important, because this allows separation of the contributions from different sources to generation and transformation of atmospheric aerosol.

The aim of these experiments was to study physical and chemical transformations in disperse systems including alkali-halide particles and atmospheric air. For this purpose, physical and chemical properties of particles were studied. Experiments on the study of transformations on a crystal surface included exposure of a disperse system to gamma rays, X-rays, or UV radiation, detection of generated substances by the methods of X-ray crystal analysis and electron microscopy, spectral studies of individual particles in the UV, visible, and infrared spectral regions.

## Experimental technique

Different methods for preparation of disperse materials are now being used in laboratory practice. We studied radiation-induced transformations using the surface of filamentary crystals. To prepare microcrystals, we used homologous series of alkali-halide salts (AHS). Filamentary crystals, microscopic single crystals, whose one dimension is many times larger than others (typical length of 1–2 mm, diameter  $\sim 1\text{--}2\ \mu\text{m}$ ), proved promising for such studies. Crystals were grown by evaporation from supersaturated aqueous solution of AHS through a porous barrier (Amelinks method), as shown in Fig. 1.

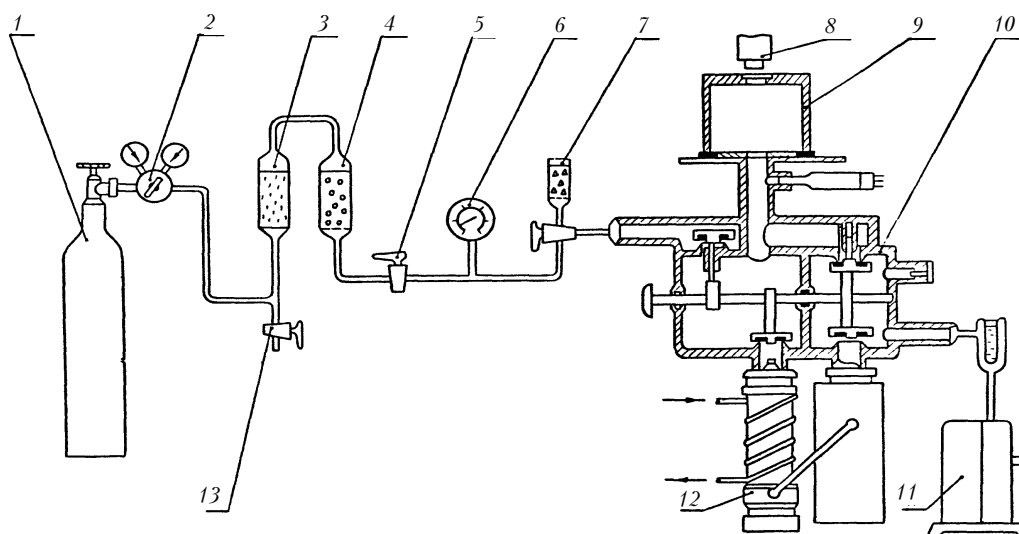
Many problems were solved with the use of samples in the form of powders. Powders were produced by mechanical grinding of salts in an agate mortar. The size of microcrystals in this case was about 2–5  $\mu\text{m}$ .



**Fig. 1.** Filamentary NaCl crystals grown by the Amelinks method (10x magnification).

### Equipment and technique of photolysis

Photolysis of crystals was studied using radiation of a filter-less low-pressure mercury lamp. Lamps of DRB-8 type with quartz cylinder (main emission bands at 185 and 254 nm) and DGRS-12 were used. For exposing to UV radiation, samples were placed 2–5 cm apart from lamps. The samples were powders and filamentary crystals poured in quartz cells.



**Fig. 2.** Reactor for irradiating and drawing replicas on the surface of samples: gas cylinder 1, reducer 2,  $\text{MgClO}_4$  dehumidifier 3,  $\text{P}_2\text{O}_5$  dehumidifier 4, vacuum cock 5, manometer 6, silica gel drier 7, X-ray tube window 8, reactor 9, distribution unit 10, roughing-down pump 11, diffusion pump 12, cock 13.

Radiolysis was studied under the exposure to X-rays and gamma rays. Radiation-induced changes on crystal surfaces were studied in wide ranges of X-ray doses, temperature, gas phase pressure, and composition of the gas phase.

The experimental setup is shown schematically in Fig. 2. The principal units of the setup include metal reactor, X-ray tube for guiding X-rays into the reactor, a system for generation of the needed composition of

the gas phase in the reactor's working volume, as well as a device for placement of samples. In the experiment, the samples were placed in the reactor and irradiated in a gas medium at a fixed composition, pressure, and temperature. The sources of radiation in our experiments were X-ray tubes.

The samples were prepared immediately after irradiation to study the surface changes in microcrystals. As this took place, the crystal temperature may vary from the temperature of liquid nitrogen to 300 K under the conditions of vacuum  $\sim 10^{-5}$  Torr. Upon completion of high-energy processing, replicas were drawn on the sample surface. For decoration, gold and carbon were precipitated onto the surface of crystals heated in vacuum up to the temperature of 600 K.

### Results and discussion

Some results of the study of interaction between atmospheric gases and vapor on the surface of alkali-halide particles are given with the allowance for their potential significance from the viewpoint of heterogeneous processes under natural atmospheric conditions.

Microcrystals of alkali-halides in the high-energy radiation fields have been studied. The exposure to high-energy radiation generates defects in the particle volume largely in the form of color centers and vacancies.

Besides, intense interaction occurs at the solid–air interface. This interaction is completed with production of a solid film on the crystal surface of salt particles. The surface layer usually includes such compounds as  $\text{HalNO}_x$ ,  $\text{MeNO}_3$ ,  $\text{MeNO}_2$ ,  $\text{MeCO}_3$ ,  $\text{MeHalO}_3$ , and  $\text{MeHalO}_4$ , where Me is alkali crystal, Hal is halide. Irradiation of nominally pure single crystals under conditions of free contact with atmospheric air is accompanied by their efficient interaction with the

products of radiolysis of the gas phase. X-ray crystal studies showed that irradiation yields synthesis of new phases (Table 1).

**Table 1. Identification of substances generated at X-ray irradiation of microcrystals in air at the temperature of 20°C. Data of X-ray crystal analysis. X-ray exposure dose of  $8 \cdot 10^2 \text{ R} \cdot \text{s}^{-1} \cdot \text{cm}^{-2}$**

Initial substance	Exposure dose, $\text{R} \cdot \text{cm}^{-2}$	Interplanar spacing $d$ , Å	New phase
KI	$3.3 \cdot 10^7$	4.5, 3.17, 2.23, 1.82	KIO <sub>3</sub>
		2.85	K <sub>2</sub> CO <sub>3</sub>
KCl	$7.2 \cdot 10^7$	3.78	KNO <sub>3</sub>
		3.30	KNO <sub>2</sub>
RbBr	$7.5 \cdot 10^7$	3.04	RbNO <sub>3</sub>
NaCl	$9 \cdot 10^7$	3.05	NaNO <sub>3</sub>
KBr	$1.0 \cdot 10^8$	3.78	KNO <sub>3</sub>
		3.30	KNO <sub>2</sub>

It is important to consider the interaction of alkali-halide microcrystals with atmospheric air in high-energy radiation fields, which can occur under actual atmospheric conditions. Atmospheric chemistry typically involves direct photochemical reactions caused by hard UV part of solar radiation and cosmic rays. At the same time, the atmosphere contains natural and anthropogenic radioactivity.

Complex laboratory studies of alkali-halide microcrystals gives us the experimental data, which can be used to explain complex processes connected with the changes in the composition, structure, and optical properties of natural marine aerosol. The results obtained can be used for supplementing the database for taking into account the contribution of marine aerosol in developing climate models. The compounds generated at hydrogenation, oxidation, and nitration of salt microcrystals intensely change the properties of aerosol. Radiation stimulates heterogeneous processes and crystallization of new compounds (nitrates, nitrites, carbonates, oxihalides). Of particular interest is stabilization of compounds like  $\text{HalNO}_x$  on the surface of salt particles and accumulation of U-centers. The above processes lead to significant changes in the optical properties of particles in the UV, visible, and infrared spectral regions. Table 2 gives the centers of the main absorption bands along with their assignment.

The results are indicative of the complex character of interactions on the surface of alkali-halide crystals during photolysis.

In the vibrational spectra of irradiated crystals, an intense absorption band in the region of 1340–1430  $\text{cm}^{-1}$  and a weaker band in the region of 600–800  $\text{cm}^{-1}$  were detected. The parameters of the spectrum are complex functions of time and conditions of irradiation and vary within wide limits. The detailed consideration reveals a nonelementary character of absorption at 1340–1430  $\text{cm}^{-1}$  due to superposition of several strongly overlapping bands. The substances causing absorption in this spectral region are likely molecular nitrogen

dioxide (NO<sub>2</sub>) and tetraoxide (N<sub>2</sub>O<sub>4</sub>), whose stretching band centers are at 1357 and 1373  $\text{cm}^{-1}$ , respectively, as well as anions NO<sub>3</sub><sup>-</sup>.

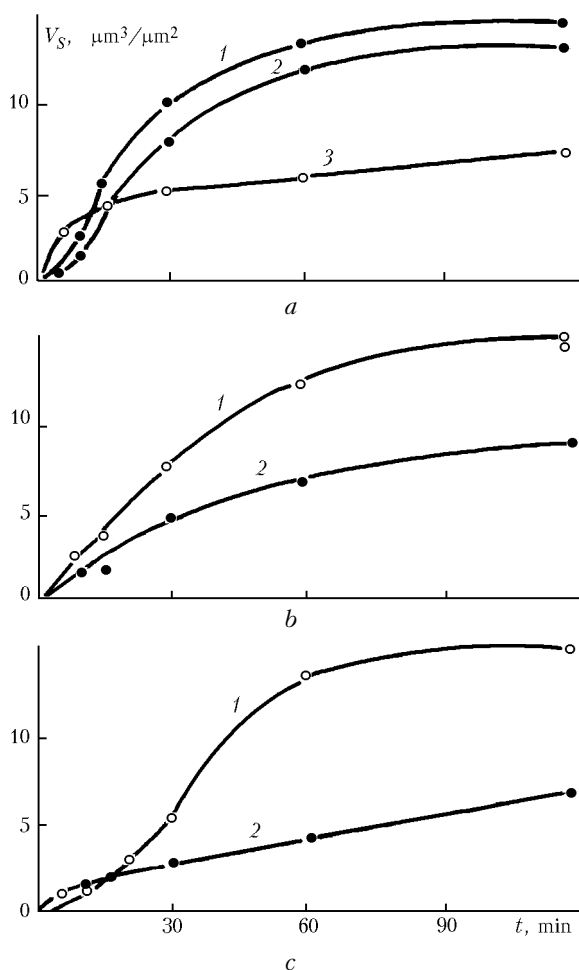
**Table 2. Identification of spectra of microcrystals after UV irradiation. Centers of the main absorption bands and their assignment**

Initial crystal	Absorption band, $\nu$ , $\text{cm}^{-1}$	Assignment
CsCl	1664	ClNO <sub>2</sub>
	1098	ClO <sub>4</sub> <sup>-</sup>
	979	ClO <sub>3</sub> <sup>-</sup>
	614	ClO <sub>4</sub> <sup>-</sup>
NaCl	1683	ClNO <sub>2</sub>
	1448	NO <sub>3</sub> <sup>-</sup>
	1365	NO <sub>3</sub> <sup>-</sup>
	1148	ClO <sub>4</sub> <sup>-</sup>
	995	ClO <sub>3</sub> <sup>-</sup>
KBr	881	NO <sub>3</sub> <sup>-</sup>
	1650	BrNO <sub>2</sub>
	1396	NO <sub>3</sub> <sup>-</sup>
	1261	BrO <sub>4</sub> <sup>-</sup>
	1014	BrO <sub>3</sub> <sup>-</sup>
	838	NO <sub>3</sub> <sup>-</sup>
KI	695	BrO <sub>4</sub> <sup>-</sup>
	646	BrO <sub>3</sub> <sup>-</sup>
	1679	INO <sub>2</sub>
	1449	NO <sub>3</sub> <sup>-</sup>
	1380	NO <sub>3</sub> <sup>-</sup>
	1272	INO <sub>2</sub>
	867	IO <sub>4</sub> <sup>-</sup>
794	IO <sub>3</sub> <sup>-</sup>	
670	INO <sub>2</sub>	

The infrared spectroscopy shows (see Table 2) that radiolysis and photolysis in all cases lead to generation of nitrates of the corresponding alkali metals. The crystal phase on the crystal surface is produced in several stages. Absorption at 1350  $\text{cm}^{-1}$  dominates at low irradiation doses; it was recorded reliably in all the studied systems with participation of KCl, KBr, KI, NaCl, and CsI. The absorption band at 1500–1300  $\text{cm}^{-1}$  for NaNO<sub>3</sub> and at 1460–1280  $\text{cm}^{-1}$  for CsNO<sub>3</sub> has a complex character. This is likely connected with the contribution of the crystal interface and the effect of these two phases on each other, as well as with numerous defects of the crystal structure. The negative feedback leads to disappearance of the  $\nu_3$  mode of the plane MeNO<sub>3</sub> molecule. Besides, redistribution of the intensity over the peaks is clearly seen for NaCl as a function of the exposure time. The results show that alkali-halide crystals interact with the ambient air, and, as this takes place, nitrates are generated already at the initial stage of transformation.

The electron-microscopy studies of the surface at irradiation of filamentary NaCl crystals showed that radiation crystallites are intensely generated on the surface of crystals. Finally, as the time of irradiation increases, a solid film is produced on the surface. The electron-microscope study of nitrate accumulation on the surface of crystals, in fact, only evaluates the process and illustrates the fact that the thickness of the crystal layer increases during irradiation. Actually, the kinetics of the process is more complicated and described by a series of sequential fast and slow stages. The study of the effect of temperature on the growth of radiation crystallites on the surface of filamentary KCl, KBr, and NaCl crystal shows that this factor affects significantly the kinetics of the process.

The electron-microscope data were used to calculate the volume of the surface phases of nitrates per unit surface of the irradiated sample. It was found that at the temperature above 320–330 K the process decelerates sharply. As the temperature of the system increases, the amount of the substance crystalizable at the dose about  $10^7$  J/cm<sup>2</sup> decreases as shown in Fig. 3.



**Fig. 3.** Radiation changes in the surface of NaCl crystal: initial crystal (a), within 5 min after irradiation by X-rays (b), and in 5 min after irradiation by X-rays (c); irradiation at different temperature (1–3);  $V_S$  is the volume of crystallites.

All the obtained data agree with the results testifying that the surface of microcrystals efficiently captures gaseous atmospheric constituents at all the considered types of high-energy exposure. In addition, it was revealed that the interaction on the surface is a complex multistage process. An essential assumption in this case is that gaseous constituents are captured with participation of the continuously refreshing water layer.

Among the results, most interesting are the following: (1) interaction of the surface with  $\text{NO}_x$ , (2) interaction with  $\text{CO}_2$ , (3) interaction with water, (4) oxidation, (5) hydrogenation of crystals, (6) crystallization on the surface of new solid phases, (7) stabilization on the surface of the compounds like  $\text{HalNO}_x$ . We have also considered some conclusions from these results that concern the study of heterogeneous processes under natural atmospheric conditions.

By now there is not a single approach to explanation of the nature of radiation processes on the surface of alkali-halide crystals and the causes of their high efficiency. Classification of these phenomena or at least separation of some group of heterogeneous interaction based on some common index is absent as well.

The reactivity of the surface of alkali-halide crystals under the exposure was many times mentioned in relation to the components of the gas phase and adsorbed substances. Irradiation of the crystal–atmosphere system leads to an intense gas–solid exchange, and the driving force may be the radiation energy absorbed in both phases. Through the sample surface, stoichiometry of crystals can be distorted with releasing the lattice components into the gas phase. This leads to halide depletion of surface layers and generation of anion vacancies. The crystal surface adsorbs gases, which then react with the base substance and form impurity phases and individual molecules of new compounds (oxides, peroxides, hydroxides, carbonates, and hydrides of alkali metals). Long irradiation leads to enlargement of the surface phases (nitrites, iodates). The anomalously high rate of radiation heterogeneous processes on model crystals was noticed in the electron microscopy, X-ray crystal analysis, and optical studies.

Under natural conditions, the same mechanisms as in the laboratory reaction may occur in atmospheric layers. They may determine the evolution of multistage physical-chemical processes on the surface of particles of marine aerosol. It is well known that atmospheric aerosol is the product of a complex set of chemical and physical processes. Because of complexity of these processes and the relatively short lifetime of aerosol, its chemical composition and physical characteristics vary widely.

The spatiotemporal variability of aerosol characteristics is high; at the same time, observations of the structure and chemical composition of particles are fragmentary. Such a situation determines low reliability

of the data on transformations of the natural aerosol, including those under the effect of natural and anthropogenic radiation factors. These factors undoubtedly manifest themselves on the global scale, affecting transformations of marine aerosol particles and, consequently, the cycles of nitrogen and chlorine compounds, ozone, carbon dioxide, and water. Radiation-chemical, photochemical, and chemical reactions responsible for transformation of aerosol components are extremely complicated and still poorly studied.

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