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FORECASTING OF FORMATION OF NITRATES IN AN ENVIRONMENT

A physical and chemical transformation surface alkali-halide micro crystal is investigated. Experiments on influence of x-ray radiation on system crystal / air are executed. Formation of firm products of heterogeneous reactions which are identified as nitrates of alkaline metals $MeNO_3$ is established. Experimental data which can optimize parameters of atmospheric heterogeneous reactions with participation alkali-halide aerosol particles are received.

Keywords: alkali-halide crystals, aerosol particles, radioactive an aerosol, x-ray radiations, heterogeneous reactions.

Salt aerosols contain particles of alkali-halide crystals. In a composition of a sea aerosol the particles of sodium chloride prevail. The strips of fundamental uptake of alkali-halides crystals lay in the field of lengths of waves less than 259 nm. Therefore contribution of a sea aerosol at the analysis of optical properties of an atmosphere, as a rule, is not taken into account. However spatial - time variability of the optical performances of an aerosol is not yet enough investigated. Sectional of examinations of hallmarks of an aerosol do not allow full to study dynamics of change of properties of particles. The chemical composition of hallmarks is studied after dissolution. An ionic composition of hallmarks therefore is analyzed more often only. In a similar situation it is difficult to receive reliable sectional concerning transformation of salt aerosols in requirements of an atmosphere. Are extremely complex and are for the present badly investigated radiochemical, photochemical and chemical reactions, which are responsible for transformation a builder of a salt aerosol.

Together with it the alkali-haloids crystals frequently will utilize as model objects in a solid-state physics. They are known as radiation-sensing crystals. Their properties under influence of ionizing radiations are rather well investigated. Idiosyncrasy of these crystals is the opportunity of making in them of dot flaws termed as centers of color-

ing. Centers of coloring can supply catalytic activity of these linking's at lengths of waves up to 800 nm. Besides it is known, that the action of ionizing radiations initiates interaction alkali-haloids crystals with builders of an environmental gas phase. In requirements of a meteorological atmosphere the containing salt aerosol, is possible to expect presence the physicochemical factors, which can give to radiation – chemical to interaction with formation of flaws of structure in volume of micro crystals and with formation on their surface of new linking's. The high-energy action gives in pinch of reactivity of crystals.

Examinations of optical properties of aerosols are one of central problems of optics of an atmosphere. The aerosol formations differ by high variability and variety. The correct account of optical properties of aerosols is necessary at the solution of manifold fundamental scientific and applied problems, bound with distribution of optical radiation in an atmosphere. The meteorological atmosphere can contain, including manifold high-energy fields, which can render essential influence on transformation of salt aerosols. Fissile use of an optical gamut of an electromagnetic radiation at system engineering of communication, detection, prompting, posting of courts, landing of planes in requirements of under visibility is impossible without knowledge of the basic legitimacies of aerosol impairment under various requirements in an atmosphere. The influence of aerosols on formation of the performances of radiation fields in an atmosphere is investigated insufficiently even in visual area of a spectrum. More often consider that the basic types, present in air, of aerosols mainly determine a dispersion of radiation in visual area of a spectrum. At transition to IR to a gamut of a spectrum on the foreground there are effects, bound with uptake of radiation.

The modern representations about optical properties of atmospheric aerosols are shaped on the basis of results of examinations in two directions. It is experimental examinations of optical properties of an atmosphere in IR of area of a spectrum and numerical model operation of the optical performances. In a basis of numerical model operation the numerical - theoretical analysis of processes of oscillation of separate types of aerosols, their transformation lays under various requirements in an atmosphere and features, caused by these processes, of optical properties of aerosols.

Mechanisms of transformation of salt aerosols depending on requirements in a meteorological atmosphere now are investigated not full enough. The role of aerosols in an atmosphere is not restricted to the essential contribution to formation of optical properties of an atmosphere. The manifold processes occurring in an atmosphere, in turn, influence a state, transformation both properties of aerosols and their property. The display of properties of atmospheric aerosols is diversiform also. There is close, but not always apparent connection of properties with changeable requirements in an atmosphere. The examinations of separate properties of aerosols will be carried out by essentially different methods. The achievements in the field of radiation chemical transformations of system crystals/air remain unused or unknowns in the field of examinations devoted to salt aerosols. In sectional operation the changes of physicochemical properties of micro crystals of alkali-halides are considered at various views of radiochemical actions. The examinations are executed in laboratory requirements. With the help of the analysis of features of uptake the particles in IR of area of a spectrum set change of their chemical composition caused by radiochemical processing.

The measuring of the optical performances of an atmosphere in «windows of a transparency» has shown an essential role of an aerosol builder in impairment of infrared radiation. Before the researchers the problem about partitioning the contribution in uptake of infrared radiation of particles of aerosols and gas builders of an atmosphere is put. Participation of an aerosol during radioactive heat exchange in an atmosphere, and also its influence on a climate and weather

are determined by spectral characteristics of uptake of an aerosol, i.e. its molecular composition. The chemical composition determines behaviors of an aerosol in a series of atmospheric processes. In natural experiments will spend a qualitative analysis of a molecular composition of an aerosol. The assembly of hallmarks in different geographical points and in different seasons allows revealing geographical and seasonal variability of the basic radiant of an aerosol. The measuring of absorption spectrums of aerosol hallmarks with particles of the various sizes will be utilized for reception of various fractions, sectional about a role, in impairment of infrared radiation, and also about mechanisms of formation of aerosol particles.

It is known, that the features of optical properties sea and oceanic of aerosols are determined by the physicochemical performances of particles, which are generated above a sea surface. Many experimental examinations of optical properties of low layers of coastal regions of an atmosphere and all atmospheric thickness are executed. The spectral characteristics of impairment, scattering indicatrix and other devices of a scattering matrix were explored. The particular dependences of these testimonials from of damp and wind mode are found out. In the field of a spectrum up to 13 microns are available sectional [1-3]. For the solution of problems of climatic monitoring the optical performances of aerosols in visual and short-range IR- area of a spectrum is most important (fig. 1).

Last years there is an accumulation of experimental dates on spatial structure of scattering factors, backscattering and impairment with the help of observations from the companions and methods of laser sounding. The absence of parallel microphysical examinations oceanic of aerosols is essential impoverish the information, gained at these measuring.

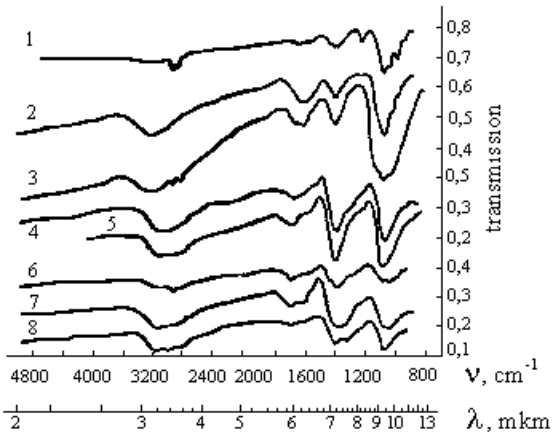

Fig. 1. Infrared spectra of tests atmospheric an aerosol [1].

Experiments on study of radioactive effects in model system particles salt/gas, that the action of short-wave radiations initiates interaction of alkali-halide crystals with an environmental gas phase. It gives in change of structure and chemical composition of particles of alkali-halides. During experiments it is revealed, that the optical properties of alkali-halide micro crystals change in ultraviolet, visual and infrared range of a spectrum. Action of small radiation doses it is enough for formation of changes of particles, which are filed by optical methods.

The alkali-halide salts are linking with a wide forbidden region capable to import the contribution to heterogeneous processes in an atmosphere [2-4]. In radioactive physics these linking are investigated rather well. They are transparent in wide spectral area. The strips of fundamental uptake of these linking lay in the field of lengths of waves less than 259 nm. Idiosyncrasy of these crystals is the opportunity of making in them of dot flaws, which term as centers of coloring. The presence of centers of coloring is easily determined by spectral methods, as gives in occurrence of absorption bands in visual area of a spectrum. Therefore such crystals get reference coloring.

The centers of coloring in these crystals can be created by various chemical and physical expedients. They are easily created at action of hard radiations. These processes are well enough investigated in radioactive

physics. However till now there is no blanket theory of making of this type of dot flaws. The interrelation of making of such flaws with character of course of heterogeneous processes stimulated by the chemical and physical factors is much worse investigated. This examination represents self-maintained interest within the framework of radioactive physics. It is known, that the centers of coloring can supply catalytic activity of these linking at lengths of waves up to 800 nm. Therefore crystals containing centers of coloring are known as photo catalytic agents.

Feature of alkali-haloids crystals is that fact, that they practically are transparent; the standing of strips of fundamental uptake is determined by chemical composition, fig. 2.

The uptake of light by the irradiated alkali-haloids crystals in ultraviolet, visual and infrared range of a spectrum essentially differs from uptake of the not irradiated crystals.

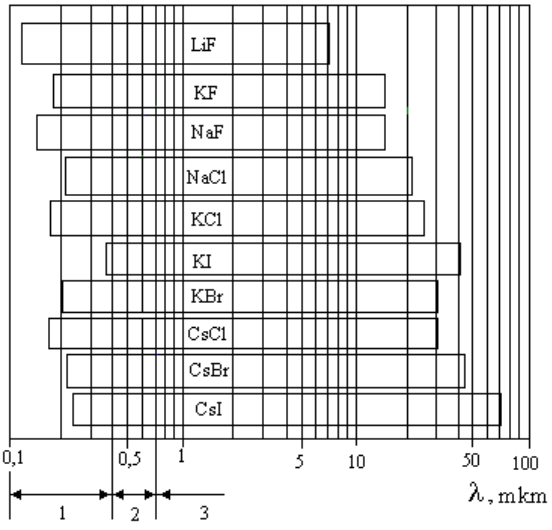

Fig. 2. Optical properties of alkali-haplide crystals in an initial state.

The natural uptake of alkali-haloids crystals (character of absorption spectrums) depends on from what the sorts by an electronic state are interlinked transitions. In alkali-haloids crystals it is possible to bleed three types of states: 1) energy bands, 2) exitons of a state, 3) local levels caused by various infringements of a lattice.

From optical transitions, bound with bands of energies, important the interzoned transitions of electrons are which is caused natural (basic or fundamental) uptake by. The strip of natural uptake of alkali-halide crystals reaches in wide area equal to several eV, and is restricted from the long-wave party to edge of natural uptake. The standing of edge of the basic uptake is determined in breadth of a forbidden region.

Idiosyncrasy of pure alkali-haloids crystals is the transparence in a wide spectral gamut in the long-wave party from edges of natural uptake down to a beginning of short-range infrared uptake caused by oscillations of a lattice, fig. 2. In the field of an energy gap the transparence can be broken by flaws of a various type: 1) impurity, 2) centers of colorings (electronic and hole).

Most typical by a type of flaws in alkali-halide crystals the impurities of stranger atoms are. The infringements of lattices caused by presence of an impurity, give in occurrence in a forbidden region of local levels of energy, and at major concentration of an impurity there are impurity bands. They cause occurrence of strips of additional uptake in the field of a transparence of a crystal. The presence of an impurity is shown not only presence of its natural absorption spectrum, but also can affect a spectrum of the basic lattice. It is expressed in bias and degradation of edge of natural uptake in crystals with major concentration of flaws, and also in occurrence of discrete absorption bands.

The activity of ionizing radiations on alkali-halide crystals gives in formation of structural flaws of a dot type, so-called centers of coloring. In spectrums of pure alkali-haloids crystals subjected activity of radiation, usually there are absorption bands caused by electronic centers (F, M, R, N, F1, K, L), hole (H, V) and excitons (α, β, γ), depending on that, electrons, the electron defects or excitons are located on structural flaws of a lattice. From all known types of radioactive flaws in ionic crystals most explored are the F-centers, which are formed in a wide temperature band from 4 up to

500oK, and which structure trusty sets (electron located by a field of anionic vacancy), table 1. Despite of intensive examinations in the field of radioactive physics, the holes centers are still insufficiently investigated. It is necessary to note, that the types of centers of coloring generated in alkali-haloids crystals under activity of ionizing radiations, their concentration substantially depend on temperature of an irradiation.

It is known, that the alkali-haloids crystals concern to group of radioactive-sensing solid bodies [5, 6]. At action the high-energy radiations in them easily create manifold structural flaws. The phenomena, bound with interaction of crystals with an environmental gas phase are less investigated which is made active by high-energy actions. All changes of structure and occurrence of new chemical combinations give that the crystals change the optical performances sharply.

Spectrometer examinations of model salt particles were utilized as a method of revealing of action of radiation at system the crystal/air. Examinations of absorption spectrums of salt particles in ultra-violet and visual area of a spectrum were carried out on a specially designed micro spectrophotometer. Thus the measuring of spectrums was carried out in areas 200-400 nm and 400-800 nm. For measuring IR of spectrums were utilized a spectrometer UR-20 and spectrometer with the Fourier by transformation of firm Perkin-Elmer. The measuring thus was carried out in areas 500-3000 cm^{-1}. For measuring IR - spectrums samples made of a powder of the relevant composition were utilized. The third effective range covers a band in infrared range of a spectrum. The occurrence of numerous absorption bands gives representation about chemical transmutations on a surface of micro crystals.

In laboratory requirements the optical properties of particles after high-energy action at system crystal/air are measured. UV, X-ray, γ - radiation and air low-temperature plasma were used as high-energy actions. The processing was spent in the field of small radiation doses with use of special instrumentation shown in a fig. 3.

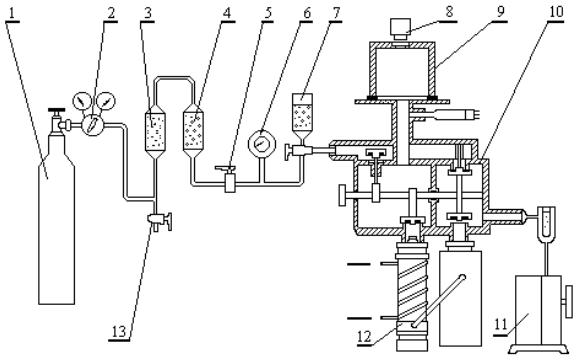

Fig. 3. The plan of experimental installation for an irradiation and drawing of retorts on a surface is model:

1 - cylinder with gas; 2 - reducer; 3 - dehumidifier MgClO4; 4 - dehumidifier P_2O_5; 5 - vacuum cock; 6 - manometer; 7 - gel; 8 - window of a X-ray tube; 9 - reactor; 10 - distributive knot; 11 - for vacuum the pump; 12 - diffusion pump.

For chemistry of an atmosphere the photochemical reactions and responses, and also responses stimulated by a natural and anthropogenesis radioactivity are important. In this connection it is necessary to expect activity of course of similar heterogeneous processes in an atmosphere with participation of a sea aerosol.

In laboratory examinations is shown, that these responses are initiated ultraviolet, X-ray and scale by radiations, and also cold air plasma. The transmutations of alkali-haloids micro crystals by methods of an electronic microscopy, IR - spectroscopy, X-ray diffraction analysis are investigated. At carrying out of experiments set, that in the specified requirements the responses on a surface and in volume of micro crystals proceeds. The heterogeneous processes cause formation and crystallization of new surface linking (nitrates, nitrites, carbonates, hydroxides), enrichment of a surface by linking such as HalNOx. Besides there is a formation and accumulation in volume F - and U – centers (table 1).

The important feature of high-energy action is the change of structure, chemical composition and optical properties of micro

crystals in comparison with an initial state. These changes are a consequence of heterogeneous responses such as solid state/gas. The sizes, structure and chemical composition of crystals, composition of a gas phase, and temperature of system, wavelength and dose of radiation determine the character and kinetics of transmutations.

Table 1.

Parameters of strips of absorption of the F-centers in alkali-halides crystals

Crystal	T=5 K, E_{max} , eV	T=300 K, E_{max} , eV
LiF	5,08	4,93
NaF	3,71	3,59
KF	2,87	2,79
RbF	2,41	2,34
CsF	1,88	1,85
LiCl	3,26	3,15
NaCl	2,75	2,65
KCl	2,30	2,20
RbCl	2,04	1,95
CsCl	2,17	2,08
LiBr	2,77	2,67
NaBr	2,35	2,26
KBr	2,06	1,97
RbBr	1,85	1,76
CsBr	1,95	1,80
LiI	3,42	3,36
NaI	2,06	2,01
KI	1,87	1,78

In a fig. 4 the absorption spectrums of crystals in ultraviolet and visual area of a spectrum, after an irradiation by Roentgen rays of system crystal/air are given at ambient temperature.

The sizes, structure and chemical composition of crystals, composition of a gas phase, and temperature of system, wavelength and dose of radiation determine the character and kinetics of transmutations. The uptake in the second gamut also characterizes a state of volume of micro crystals and is caused by formation of centers of coloring - F-centers. The absorption constants in the relevant strips depend first of all on radiation doses, from chemical composition and from the sizes of micro crystals, composition of a gas phase and other factors. The third gamut grasps a band in infrared range of a spectrum and the occurrence thus of absorption bands gives representation about chemical transmutations on a surface of micro crystals. Occur thus more often strip, bound with uptake by ions NOx- or linking HalNOx.

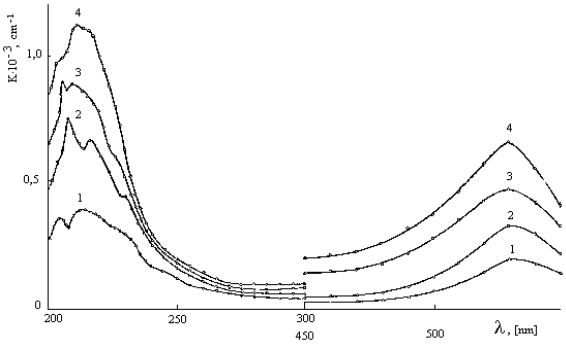

Fig. 4. Absorption spectrum of crystal KCl. The thickness of a crystal makes 19 mkm. The irradiation by x-rays of system crystal/air is spent at 15^0C during. An irradiation during 120 minutes corresponds to a dose $7{,}2 \cdot 10^7$ P cm^{-2}: 15, 30, 60, 120 mines (curves 1, 2, 3, 4, accordingly)

In a fig. 5 the IR-spectrums are submitted is model crystal, handled x-ray radiation.

The characteristically sharp change of the optical performances of micro crystals is visible from the table 2 (for all views of high-energy action). Spent conjugate to optical measuring x-ray diffraction and electromicroscopic of examination have shown presence of close interrelation between influence of radiations and display of transformation of properties of particles of alkali - halide salts [7].

Experimental methods (weighing is model, X-ray diffraction examinations, the measuring IR of spectrums) allow spending study of heterogeneous responses at processing by plasma of system micro crystal/air.

The opportunity of application of experimental dates about the mechanism of heterogeneous transmutations in system alkali-halide crystal/air in physics of aerosols and optics of an atmosphere surveyed. The mod-

els of an aerosol set by a gang of values of the optical performances of aerosols, do not allow those or otherwise compared with a particular situation in an atmosphere to sweep all possible situations. A radiant of optical models, sectional for build-up, are or files of results of experimental optical measuring in natural requirements, or results of numerical calculations. Between these basic directions in model operation there is a considerable disruptor.

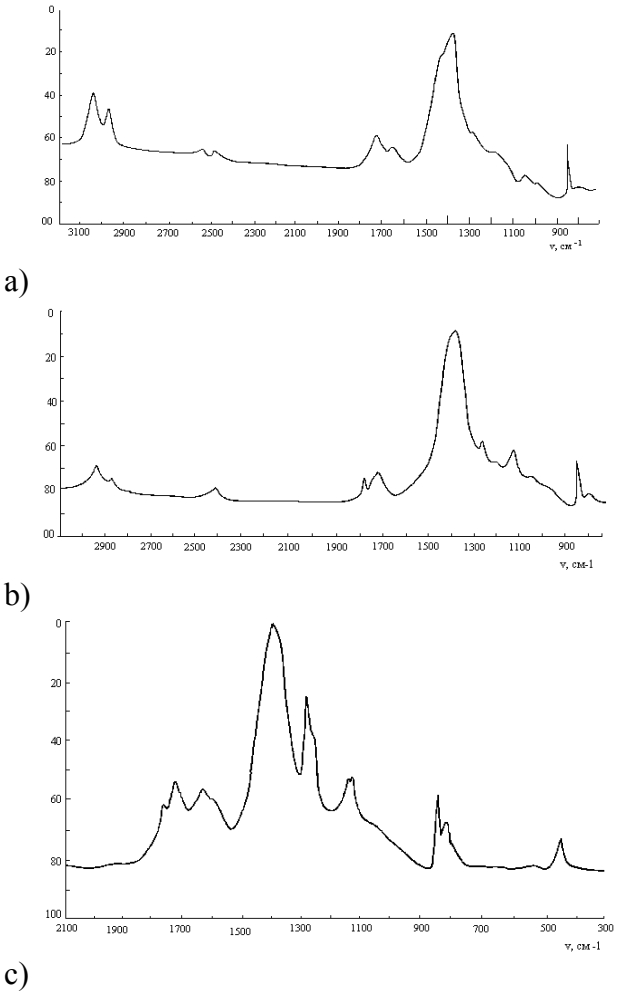

Fig. 5. IR-spectrums is model after an irradiation by x-rays of system crystal/air at ambient temperature, dose $5.0 \cdot 10^7$ P· cm^{-2}:
NaCl (a), KCl (b), KBr (c)

Only complex use modern sectional about optical and physical properties of aerosols, about physical processes determining their transformation in requirements of an atmosphere, allows coming nearer to the solution of a problem of build-up of enough complete and reliable optical model of a salt aerosol.

Table 2
Identification of the substances formed at x-ray irradiation

Initial crystal	Exposition dose, P	Absorption band of IR-spectrum, ω, cm^{-1}	Interpretation of strips in IR-spectrum
NaCl	$5{,}4 \cdot 10^7$	1460, 840	CO_3^-
		1260, 1380	NO_2^-
KCl	$4{,}3 \cdot 10^7$	1360, 835	NO_3^-
		1260,1380	NO_2^-
		1080, 1140	ClO_4^-
KBr	$6{,}3 \cdot 10^7$	1390, 840	NO_3^-
		1280, 1360, 810	NO_2^-
		790	BrO_3^-
KI	$2 \cdot 10^7$	760	IO_3^-
		1460, 840	CO_3^-
		1260, 1380	NO_2^-
RbBr	$4{,}7 \cdot 10^7$	1380, 835	NO_3^-
		1270, 1380	NO_2^-
		790	BrO_3^-
		1460, 840	CO_3^-

For chemistry of an atmosphere the photochemical reactions and responses, and also responses stimulated by a natural and anthropogenesis radioactivity are important. In this connection it is necessary to expect activity of course of similar heterogeneous processes in an atmosphere with participation of a salt aerosol.

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