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RADIATION INDUCED OPTICAL PROPERTIES OF FERROELECTRIC CRYSTALS

Abstract: In the paper results of the study of $[(CH_3)_4N]_2CuCl_4$ and $(CH_3)_3NHCdCl_3$ crystals are presented. The absorption spectra in the visible region of these compounds, so nonirradiated, as well as γ, X-irradiated have been discussed. The processes forming irradiation defects in crystalline structures are analyzed.

Introduction

Different external influences often result in changes of optical spectra of crystals. This, in particular, concerns photochromic and radiation induced changes of optical parameters. The results of complex investigations of the above phenomena in representatives of A_2BX_4 and ABX_3 groups of crystals are described in this work.

A variety of optical changes influenced by ionizing radiation exists; they can appear even at a weak irradiation. The presence of defects in the crystal lattice results in the formation of additional levels in the forbidden area. Defects, which are responsible for additional absorption bands, are the centers of coloration. In our case one should consider the electronic centers which form energetic levels higher than the middle ones of the forbidden area.

Changes in $(NH_4)H_2PO_4$ (ADP) crystals , which were caused by action of ionizing radiation, as well as changes in other representatives of KH_2PO_4 (KDP) group, differ by their conformity to laws. Sometimes however the contribution to absorbed dose of radiation is not different. There exist similar changes in position of Curie point, spontaneous polarization, mobility of domain walls in the electric field, anomalies of electro-physical properties near a phase transition point [1]; the additional bands of optical absorption are appearing. The above reasons allow, only from this point of view, to consider structural sensitiveness of crystals of the given group. Information about energetic changes of absorption coefficient of the γ-quanta in a crystal allows to estimate contribution of its separate structural elements to interaction with γ-quanta of a different energy.

Experimental

Investigated $[(CH_3)_4N]_2CuCl_4$ (TMA-CuCl$_4$) and $(CH_3)_3NHCdCl_3$ (TrMA-CdCl$_3$) crystals were grown from aqueous solution of the corresponding salts taken in stoichiometric amounts, by the method of slow evaporation at room temperature. The TMA-CuCl$_4$ crystals with the admixture of gadolinium, *i.e.* TMA-CuCl$_4$+Gd^{3+} crystals were obtained by adding GdCl$_3$ to TMA-CuCl$_4$ aqueous solutions. The best growth conditions were in the presence of chloride ions excess.

ADP crystals were also investigated. At temperatures below the temperature of phase transition Tc = 147 K they are antiferroelectrics with orthorhombic symmetry (point group 222); at higher temperatures they are attributed to the tetragonal spatial group (point group 42m).

In the study of ADP crystal, the bunch of γ-rays was concentrated by leaden collimator and spread parallel or athwart to its optical axis. Isotopes from a set of exemplary spectrometric gamma-emitters served as sources of γ-irradiation. The range of energies was from 59 keV (^{241}Am) to 1836 keV (^{88}Y).

For the irradiation by X-rays, units with Mo-tube (U = 40 kV, I = 13 mA) and Cu-tube (U = 30 kV, I = 18 mA) were used. The Raman spectra were registrated using a modified DFS-52M diffraction-photospectrometer.

Results and discussion

The considerable changes after the irradiation by X-quanta were observed in UV spectra of TrMA-CdCl$_3$ crystals. (Fig. 1). For high exactness of measurements, the experiments were conducted in the unpolarized light. With decreasing wavelength, *k* increases to a value of 25 cm^{-1} at 230 nm. After X-irradiation during 5,25 hours, beginning with 450 nm, the absorption coefficient *k* rapidly increases and is equal to 40 cm^{-1} at 230 nm.

Dependence of absorption coefficient for different wavelengths on X-irradiation time is given on the insert of Fig. 1. As one can see, for different wavelengths the character of change of absorption coefficient *k* at the increasing irradiation doses remains almost identical. The dose of irradiation, and accordingly concentration of defects, is determined by the irradiation time. Therefore, instead of the term the «dose of irradiation» it is possible to use the term «time of irradiation» *t* [2]. The wavelengths for which the time dependence of absorption coefficient was studied, were chosen in such a way, that the absorption bands were within their values. Increase of intensity of these bands after irradiation, results in the increase of quantity of defects in the crystal. One should mention the faster increase of absorption coefficient for the X-irradiated crystal at λ = 350 nm as compared with other wavelengths.

The absorption spectra of nonirradiated and X-irradiated during 2 hours (TMA-CuCl$_4$) crystals as well as TMA-CuCl$_4$+Gd^{3+} crystals are presented in Fig. 2. In TMA-CuCl$_4$ crystals the region of transparency is 520–680 nm. After the irradiation the intensity of absorption bands grows and the maximum of absorption band is displaced into the long wavelength region. Ultraviolet absorption edge shifts to the side of long wavelengths. The spectrum of irradiated TMA-CuCl$_4$+Gd^{3+} crystals is similar to that of TMA-CuCl$_4$.
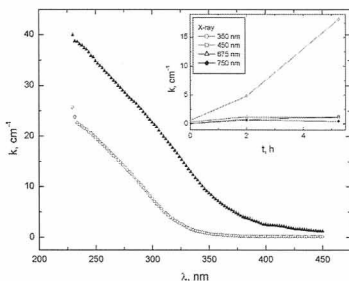
Fig. 1. Nonpolarized UV absorption spectra for the nonirradiated and X-irradiated TrMA-CdCl$_3$ crystals (Mo-tube, U = 40 kV, I = 13mA, t_{irr} = 5 h). Insert shows the dependence of the absorption coefficient for different wavelengths on the time of X-irradiation

▲ ▲ ▲ irradiated TrMA-CdCl$_3$
○○○ nonirradiated TrMA-CdCl$_3$
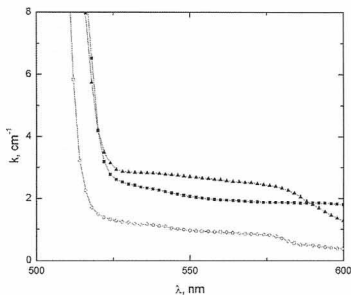
Fig. 2. Absorption spectra of nonirradiated and X-irradiated TMA-CuCl$_4$ crystals (Cu-tube, U=30 kV, I=18 mA, t_{irr}=2 h) for the light polarization along the *b* axis as well as TMA-CuCl$_4$+Gd^{3+}crystals

▲ ▲ ▲ X-irradiated TMA-CuCl$_4$
○○○ nonirradiated TMA-CuCl$_4$
■ ■ ■ X-irradiated TMA-CuCl$_4$+Gd^{3+}

To find reason of defects appearence in crystals during X-radiation, the absorption for "hard" radiation in ADP crystals was studied. It was found that the changes resulting in crystals considerably affected their both macroscopic and microscopic properties.

In the investigated range of energies it is possible to see all effects which occur in absorption of γ-rays, in particular photoeffect, compton dispersion and effect of formation of electron-positron pairs.

Dependence of weakening coefficient μ for γ-quanta along and perpendicular to the optical axis of crystal ADP on the irradiation energy is presented in Fig. 3.

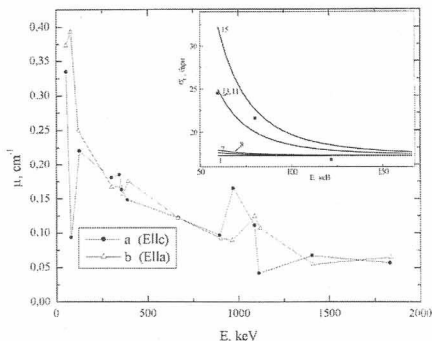**Fig. 3.** Dependence of weakening coefficient μ for γ-quanta in crystals ADP along (a) and perpendicular (b) to optical axis on the energy of irradiation. Insert shows energy dependence of effective section of a photoeffect σ_τ for the γ-rays propagation perpendicular to the optical axis of ADP crystal; the numbers are values of an effective charge at extrapolation according to the formula 3

One can see, that within the limits of exactness of experiment, the character of this dependence $\mu(E)$ practically is not influenced by the direction of X-rays distribution. When energy value is increasing, μ decreases from 0,36 cm^{-1} at $E = 59$ keV to 0,08 cm^{-1} at $E = 1836$ keV, according to a nearly exponential law.

When passing through the matter, the interaction of γ-quanta with its atoms occurs, and they lose part of the energy, changing direction of distribution. Such quanta leave the bunch. Mainly three effects stimulate weakening of γ-quanta bunch: photo-electric absorption, compton dispersion and formation of electron-positron pairs. Complete coefficient of weakening is described as:

$$\mu = \tau + \sigma + \chi \tag{1}$$

where τ – coefficient of weakening due to a photoeffect;

   σ – coefficient of weakening due to compton dispersion;

   χ –coefficient of weakening due to formation of electron-positron pairs.

Contribution of these processes in particular energy areas of γ-quanta is different, for example the photoeffect prevails in the area of low energies (to 100 keV), and other processes may be neglected. We took exactly this area of low energies for subsequent consideration.

As it is known [3], effective crossing σ_τ process of weakening, calculated for one atom of matter, is determined as

$$\sigma_\tau = \frac{\mu A}{\rho N_a},\tag{2}$$

where A – atomic weight of elements which the matter of absorber consists of;

ρ – density;

N_a – Avogadro constant.

Photoelectric absorption can be taken into account according to a formula

$$\sigma_\tau = \Sigma_0\, 4\sqrt{2}\,\frac{Z_{e\phi}^5}{137^4}\left(\frac{mc^2}{E}\right)^{7\!/\!2}\tag{3}$$

where $\Sigma_0 = \dfrac{8\pi}{3}r_0^2$ – classic coefficient of Thomson's dispersion for a lone electron;

$r_0 = \dfrac{1}{4\pi\varepsilon_0}\dfrac{e^2}{mc^2} = 2{,}818\times10^{-15}$ cm – classic radius of electron.

Theoretical dependences of the effective crossing of photoeffect, calculated with formula 3 for atoms of all elements contained in ADP molecule are given in Fig. 3 (insert). The experimental points, obtained by the calculation of coefficient of weakening with a formula (2) are also shown. The insert in Fig. 3 indicates that the best compatibility of theoretical and experimental results is observed at $Z_{e\phi} = 13{,}11$. Among chemical elements of the ADP molecule, phosphorus $^{32}_{15}\mathrm{P}$ has the nearest to 13,11 value of atomic number. It is noteworthy that main weakening of γ-quanta bunch in the range of considered energies (50–100 keV) occurs due to a photoeffect exactly on phosphorus atom. At the same time, from data of EPR study [4] and results of neutron experiments [5], all changes in the crystals of KDP group are caused by the break of hydrogen bonding. This break can result from the rapid secondary electrons, which appear in the process of photo-weakening on the phosphorus atoms. They destroy hydrogen bonding after the direct collisions with the hydrogen atoms, leading to formation of microscopic local defects.

We will consider a similar situation on the example of formation of the radiation induced defects in TrMA-CdCl₃ crystals. The changes can be explained by formation in the crystalline structure of color centers (F-centers, or anionic vacancies, which take in electrons). Nature of additional absorption bands in the TrMA-CdCl₃ crystal under action of X-quanta of electromagnetic radiation is explained as follows. Vacancy in place of the knocked out chloride ion is substituted by an electron (Fig. 4). Approximately, the same forces, which act on the chloride ion, act on this electron. But at identical forces, the squares of vibrations frequencies are inversely proportional to masses. It is known that the electron is approximately 62000 times lighter than the chlorine atom. Therefore, the vibrations frequency of electron, which occupied a vacancy, will be larger than the vibrations frequency of the chlorine atom. This is sufficient for the presence of electron's vibrations frequency in visible region.

Force which retains an electron in position of equilibrium must have the character of quasi springy force; its dependence on displacement of electron is determined by a law:

$$F = -br \qquad (4)$$

where b – the proper constant of resilient communication.

Experiments have confirmed that properties of atom may be described by properly applied classic laws. In particular, one may describe interaction of an atom with a light wave if one considers the atom as an aggregate of harmonic oscillators of the proper frequency, *i.e.* that an electron is bound in the atom by quasi springy force F. Thus, equation of motion of electron with a mass m, which is displaced from position of equilibrium, is:

$$m\ddot{r} = -br \qquad (5)$$

and

$$r = r_0 \cos\omega_0 t \qquad (6)$$

where r_0 – amplitude, and $\omega_0 = \sqrt{b/m}$ – frequency of own vibrations of electron, thus ω_0 depends on the nature of atom, which determines the size of constant b. In our case $b \approx 16$ kg/s^2 for $\lambda = 445$ nm. Thus, the X-irradiation of TrMA-CdCl$_3$ crystals causes formation of defects, which stimulate appearance of absorption bands in the visible region.

The increase of coefficient k for the X-irradiated crystals in the whole visible region can be also connected with partial radiation destruction of organic cation.
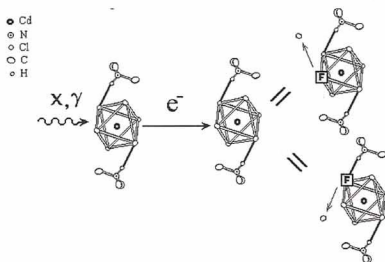

Fig. 4. Model of the F-centers forming in X-irradiated TrMA-CdCl$_3$ crystals

The fact that an electron is knocked out from the chlorine atom was confirmed by Raman spectra. Raman spectra of nonirradiated and X-irradiated TrMa-CdCl$_3$ crystals are given in Fig 5. In the spectrum of nonirradiated TrMA-CdCl$_3$ crystals the bands with maxima at 175, 220 and 800 cm^{-1} are the most intensive. Bands in a range 300–1000 cm^{-1} are responsible for oscillation of C-N-C bond. Internal vibrations of chain of octahedrons Cd–Cl occur in the range of 100–250 cm^{-1} [6]. Band which has a maximum at $\nu = 26$ cm^{-1},

is related to antiphase of chain of octahedrons, and the band in a range $\nu = 38 \div 40$ cm^{-1} results from translational and rotatory oscillations of TrMA group.

In Raman spectrum of TrMa-CdCl$_3$ crystal, X-irradiated during 5,25 h (Fig. 5), additional bands are not observed, but a considerable decrease of intensity of bands, which are responsible for symmetric tension of C–N–C bond (800 cm^{-1}), and also for antisymmetric deforming vibrations of Cd–Cl group (175 cm^{-1}) takes place. Stability of bands resulting from X-radiation shows that the structural complex TrMA does not collapse. Decrease of intensity of bands of some frequencies indicates that the number of bonds, responsible for these frequencies, is lower. It can be suggested that the electron, knocked out by X-quantum from cadmium, replaces the chloride ion. This fact results in weakening of net of hydrogen bonds like a N–H⋯Cl, which are responsible for deformation of separate structural groups of crystal, in particular – Cd–Cl.
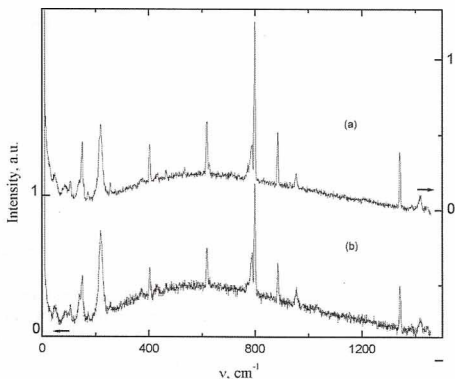
Fig. 5. Raman spectra of the nonirradiated (a) and X-irradiated (b) during 5,25 hours
TrMA-CdCl$_3$ crystals (at $T = 295$ K)

Absorption spectra of nonirradiated and X-irradiated TrMA-CdCl$_3$ crystals are presented in Fig. 6. One can see that the nonirradiated crystal is practically transparent in a range of 400–750 nm, only at 445 nm and 670 nm there are small bands with $k_{max} \approx 0,4$ cm^{-1}. With increase of wavelength the absorption coefficient sharply increases, approaching to the infrared (IR) edge of absorption. The X-irradiation of crystals during 5,25 h results in the absorption increase in the region of transparency; the bands within the range of 420–500 nm and of 610–700 nm appear. The maximal value of absorption coefficient k reaches level of 1,2 cm^{-1}. The edge of IR absorption shifts to the short wavelength region, and already at 740 nm the increase of k is observed, while for the nonirradiated specimen this increase begins with 760 nm.
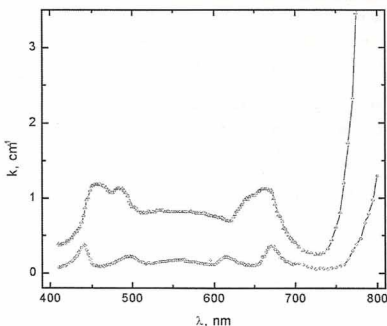
Fig. 6. Spectra of optical absorption of the nonirradiated and X-irradiated TrMA-CdCl$_3$ crystals for polarization of light E$\|$ b
$\triangle\triangle\triangle$ X-irradiated TrMA-CdCl$_3$
$\circ\circ\circ$ nonirradiated TrMA-CdCl$_3$

Conclusions

The present work shows results of the study concerning nonirradiated and γ-, X-irradiated crystals. Besides the description of the obtained spectral dependences, processes of defect forming within the crystalline structure are analyzed.

Theoretical dependences of the effective crossing of photoeffect have been calculated for atoms of all elements, contained in ADP. The experimental points, obtained by calculation of coefficient of weakening are also shown. The best compatibility of theoretical and experimental results is observed at Z_{ef} = 13,11. Among chemical elements, contained in ADP, phosphorus $_{15}^{32}$P has the nearest to 13,11 value of atomic number.

It is noteworthy that main weakening of γ-quanta bunch in the range of considered energies (50–100 keV) takes place due to a photoeffect exactly on phosphorus atom.

We have measured the absorption spectra of TMA-CuCl$_4$, TMA-CuCl$_4$+Gd^{3+} and TrMA-CdCl$_3$ crystals in the visible region for the direction of light propagation along the b-axis and for the polarization along the a- and c crystals axes, as well as the absorption spectra of nonpolarized light for the nonirradiated and β-, γ-, X-irradiated samples.

Various kinds of absorption band shifts within the visible region for the radiationally damaged samples have been observed; these spectra were compared to those of non-irradiated samples. The shift of the absorption edge as well as the additional absorption bands within the visible region for the irradiated samples have been observed. The magnitude of the shift depends on the type and dose of irradiation. As a rule, upon irradiation the absorption edge shifts to the long wavelength spectral range, but after the 70-hours action of β-particles upon the crystal, we could observe the shift of UV-edge to

the short wavelength range. This fact may be explained by electron-stimulated diffusion of the particles during mechanical structural damages.

A model for F-centers under the action of X-rays is proposed, the essence of which is as follows: the quant impinging on the crystal knocks out the electron from cadmium, which, in turn, knocks chlorine atom out of the lattice. The chloride ion gets into the internode, while the electron gets in place of the chlorine atom. This assumption is to a certain degree corroborated by absorption spectra and by Raman scattering spectra of the TrMA-CdCl$_3$ crystals.

Our research confirmed the fact that spectral techniques are effective tools in the study of irradiation defects in ferroelectric crystals.

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WŁAŚCIWOŚCI OPTYCZNE KRYSZTAŁÓW FERROELEKTRYKÓW INDUKOWANE PROMIENIOWANIEM

Streszczenie: W artykule podano wyniki badań kryształów [(CH$_3$)$_4$N]$_2$CuCl$_4$ i (CH$_3$)NHCdCl$_3$. Przeprowadzono dyskusję widm absorpcyjnych w zakresie widzialnym tych związków, zarówno przy działaniu γ i X promieniowania, jak też bez promieniowania. Ponadto podano analizę procesów tworzenia defektów w sieci krystalicznej, spowodowanych wpływem promieniowania.