Multiphoton and impurity photoconductivity of alkali halide crystals excited by picosecond laser pulses

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An investigation was made of the photoconductivity of wide-gap KCl, NaCl, KBr, and KI crystals excited by picosecond pulses of the fourth, third, and second harmonics of a YAG:Nd laser. The processes of multiphoton excitation of nonequilibrium carriers were detected and identified right up to the fourth order inclusive and measurements were made of the corresponding multiphoton absorption coefficients. The drift mobilities of thermalized electrons in the conduction band were determined. A study was made of the influence of high-temperature heating of crystals on the impurity photoconductivity and of the relationship of this photoconductivity to the processes of damage of alkali halide crystals by picosecond laser pulses.

INTRODUCTION

Generation of nonequilibrium carriers in wide-gap insulators is becoming increasingly important in tackling a number of important problems in quantum electrons and solid-state physics, among which we might mention the development of bistable optical elements, construction of color-center lasers, formation of radiation defects in crystals, and optical stability of transparent materials, particularly in the ultraviolet part of the spectrum. It is especially interesting to study the fundamental (interband) processes of excitation of nonequilibrium carriers as a result of multiphoton absorption of light in crystals.

The first attempts to detect multiphoton excitation of nonequilibrium carriers in wide-gap insulators were made by Dneprovskiĭ *et al.*[1] and by Aseev *et al.*,[2] followed later by Catalano *et al.*[3] These authors investigated the photoconductivity of wide-gap (including alkali halide) crystals excited by ruby ($\lambda = 0.694$ μm) and neodymium ($\lambda = 1.06$ μm) lasers and their harmonics ($\lambda = 0.347$ and 0.53 μm) in the form of millisecond and nanosecond pulses with a spatially inhomogeneous (multimode) distribution of the radiation intensity, but they interpreted the results incorrectly as manifestation of multiphoton (up to the sixth order!) processes of generation of nonequilibrium carriers. The cross sections for multiphoton absorption of light obtained in Ref. 3 were also unreliable, with the exception of the two-photon absorption cross section of KI, close to that obtained later[4] by direct measurement of the absorption of light. One could say that, before the publication of Refs. 5, 6, and 7, there were no published reliable reports of the discovery of multiphoton (of order $k > 2$) processes of excitation of nonequilibrium carriers or of measurements of the corresponding optical absorption coefficients of wide-gap crystals (the literature can be found in the review of Nathan *et al.*[8]) The exciton luminescence of KI crystals was excited at $T = 88$ K by the absorption of the second harmonic of a picosecond YAG:Nd laser ($\lambda = 0.532$ μm), and the three-photon absorption cross section was determined.[5] A photoacoustic method was used[6] to determine the four-photon absorption cross section of the same radiation in NaCl, whereas Ref. 7 reported measurements of the three- and four-photon absorption coefficients of KCl and NaCl by the method of picosecond laser photoconductivity. It should be pointed out that the use of picosecond pulses made it possible to determine[4–7] the coefficients (or cross sections) of multiphoton absorption of light in wide-gap insulators. This was because the threshold intensity of laser damage to transparent materials in the case of picosecond pulses was considerably higher (by at least an order of magnitude) than in the case of nanosecond pulses, which made it possible to excite and record reliably multiphoton processes in a wide range of intensities under such conditions that the prebreakdown phenomena were unimportant.

The method of picosecond laser photoconductivity had been employed also[9] to investigate photoexcitation of carriers in wide-gap insulators and to measure the lifetimes of nonequilibrium carriers in KBr, NaF, and Al_2O_3 crystals excited by picosecond pulses of the second harmonic of a ruby laser.

Our aim was to investigate in detail the processes of photoexcitation of nonequilibrium carriers in alkali halide crystals by picosecond laser pulses, to measure the multiphoton absorption coefficients and carriers mobilities for these crystals, and to study the impurity photoconductivity and its possible relationship to the laser damage processes.

APPARATUS

Our experiments were carried out using a specially developed YAG:Nd^{3+} laser system characterized by an improved stability of the spatial, temporal, and energy parameters of the high-power radiation pulses and by high (tens of percent) efficiencies of conversion of the fundamental frequency ($\lambda = 1.064$ μm) into the second, third, and fourth harmonics, while retaining the spatial homogeneity of the beams.[10]

The time structure of the laser pulses at all four emission wavelengths was investigated using an image converter. The profiles of the pulses were nearly Gaussian. The pulse duration at the fundamental frequency was 55–60 ps, whereas at the harmonic frequencies the pulse duration decreased by a factor of $n^{1/2}$ (where n is the number of the harmonic). The spatial distribution of the intensity in the beams (measured using a detector based on a charge-coupled device structure) was also Gaussian. The energy measurements were carried out using a calibrated pyroelectric calorimeter and photodiodes which were calibrated using this calorimeter.

The photoconductivity signal was recorded as shown

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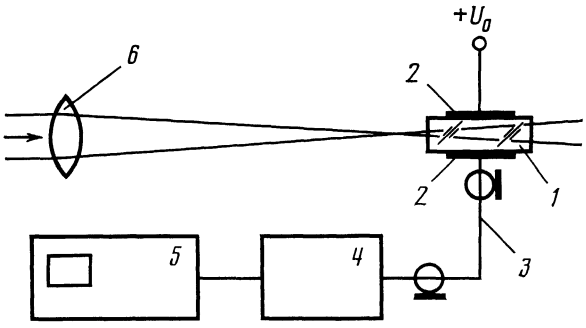

FIG. 1. System used to record the photoconductivity signal: 1) sample; 2) electrodes; 3) cable line; 4) amplifier; 5) oscilloscope; 6) lens.

schematically in Fig. 1. Samples of the investigated crystals were split along cleavage planes and had dimensions of $3\times15\times18$ mm; they were placed between electrodes subjected to "bell-shaped" voltage pulses of 100 μs duration and amplitude U_0 up to 4 kV (as in Ref. 11) synchronized with the exciting radiation. The signal passed along a cable line with a wave impedance $R = 50\ \Omega$. It was recorded with a wide-band oscilloscope directly before or after amplification. The recording system was carefully screened so that the interference noise did not exceed 1 mV in a band of 0–500 MHz. The time resolution determined and the linearity of the whole recording channel was checked in a special investigation of its transient characteristic using an optical rectification signal. This was done by placing an $LiNbO_3$ crystal between electrodes and inducing in this crystal an optical rectification signal resulting from the interaction with two laser pulses of the same intensity (and of $\lambda = 1.064$ μm wavelength) with the delay between them varied within the range 0–5 ns. Since the duration of the optical rectification signal was practically equal to the duration of the exciting radiation,[12] the recording channel generated two identical picosecond electrical pulses. In a study of the dependences of the amplitude and profiles of the pulses recorded by the oscilloscope on the delay time it was possible to determine in each specific case the transient characteristic time of the recording channel and to estimate the maximum resolution of the system, which in our case was ≈ 100 ps.

Special attention was given to suppression of the influence of the surface photoconductivity by making the samples several millimeters larger than the electrodes and heating the samples constantly to 80°–60°C with a halogen lamp or with dry air. Moreover, the influence of the electrodes was eliminated by preventing direct or scattered laser radiation from reaching them. The profile of the signal was evidence of the absence of these stray effects. The surface conductance and the electrode signal had a characteristic irregular profile with the duration 5–10 times greater than the duration of our useful signal. A considerable influence on the photoconductivity signal was exerted also by the creation of radiation defects (F centers) as a result of the interaction with laser radiation. All the measurements were therefore carried out so that a given part of a sample was irradiated only once in order to eliminate the accumulation effect. The intensity of the exciting radiation was enhanced by compression of the beam with a long-focus lens so that its diameter on the surface of a crystal was 0.3–1 mm.

MEASUREMENT METHOD

The multiphoton absorption coefficients were determined by comparing the photoconductivity signals with those resulting from two-photon excitation of nonequilibrium carriers when the two-photon absorption coefficients (determined directly from the absorption of light[4]) were known. This approach enhanced the precision of the measurements because it eliminated some indeterminacy associated particularly with the geometry of the interaction region and with the characteristics of the channel used to record the photoconductivity signal. It should also be mentioned that direct experiments yielded the total number of the electrons in the interaction region, which was proportional to the absorbed energy, and this was used to find the absorption coefficients.

Let us assume that a sample of length l is subjected to a laser pulse with an intensity distribution $I = I(r,z,t)$, where r and z are the transverse and longitudinal coordinates, and t is the running time. It follows from the definition of the k-photon absorption coefficients β_k that

$$\frac{1}{I}\frac{dI}{dz} = -\sum_{k=1} \beta_k I^{k-1}.$$

In the case of weak absorption, i.e., when the condition

$$\beta_k I^{k-1}(r, 0, t)\, l \ll 1$$

is satisfied, the total number of electrons N_k formed in the conduction band of a crystal as a result of k-photon absorption can be described by

$$N_k = n_k V_k, \tag{1}$$

where $V_k = \pi r_k^2 l$ is the effective volume, r_k is the effective radius of the interaction region, and n_k is the effective electron density.

In the case of a Gaussian pulse with the intensity distribution

$$I(r, 0, t) = I_0 \exp(-r^2/r_0^2) \exp(-t^2/\tau^2)$$

these parameters are given by

$$r_k = \frac{r_0}{k^{1/2}}, \quad V_k = \frac{\pi r_0^2 l}{k}, \quad n_k = \beta_k \frac{I_0^k}{k\hbar\Omega} t_k, \tag{1'}$$

where Ω is the frequency of the exciting light and $t_k = \tau(\pi/k)^{1/2}$ is the effective duration of the pulses. (It should be noted that the pulse duration is defined here as the quantity $t_l = \pi^{1/2}\tau$, so that the energy of a pulse is $W = I_0 \pi r_0^2 t_l$.) The equivalent electric circuit of the method used by us to record the photoconductivity signal consisted of a capacitor C, representing the electrodes with the sample between them, connected in series with a load resistance R and fed by a dc voltage U_0.

We shall now write down the expression for the charge density $\rho(\mathbf{r})$ formed as a result of k-photon generation of carriers and their drift in an external field:

$$\rho(\mathbf{r}) = \rho_k \{\exp(-\mathbf{r}^2/r_k^2) - \exp[-(\mathbf{r}-\mathbf{a})^2/r_k^2]\}, \tag{2}$$

where $\rho_k = en_k$ is the effective charge density, e is the electron charge, and $\mathbf{a}$ is the drift displacement of the charges. Equation (2) ignores, for the time being, the processes of carrier recombination and screening. Let Q be the charge on

the capacitor electrodes, so that the potential u across the electrodes can be written in the form

$$u=\frac{Q}{C}-\frac{V_k}{V}\frac{S}{C}\rho_k a, \tag{3}$$

where the electric field along the axis of the interaction region is given by

$$E(0)=\frac{Q}{CL}-\eta\frac{S}{CL}\rho_k a. \tag{4}$$

Here, S is the electrode area, L is the distance between the electrodes, $V=SL$, and η is a dimensionless parameter given by

$$\eta=1+2\frac{V_k}{V}-\frac{\pi^2}{3}\frac{r_k^2}{L^2}+\ldots \tag{5}$$

Equations (3)–(5) are obtained by the method of inclusion mapping in the approximation of a parallel-plate capacitor, subject to the additional conditions $a\ll r_k$ and $V_k\ll V$ known to be satisfied in our case. We shall also allow for the process of linear recombination of carriers with a characteristic time τ_r, i.e., we shall assume that

$$\rho_k(t)=\rho_k\exp(-t/\tau_r).$$

The number of carriers per unit volume recombining in a time dt is

$$n_k\exp\left(-\frac{t}{\tau_r}\right)\frac{dt}{\tau_r}.$$

These carriers "determine" the charge displacement $a(t)$. Therefore, it follows from the superposition principle that

$$u=\frac{Q}{C}-\frac{V_k}{V}\frac{S}{C}\rho_k\left[\int_0^t a(t)\exp\left(-\frac{t}{\tau_r}\right)\frac{dt}{\tau_r}+a(t)\exp\left(-\frac{t}{\tau_r}\right)\right]. \tag{6}$$

We can similarly rewrite Eq. (4) by replacing a with the expression in the square brackets of Eq. (6). By definition, we have

$$d\mathbf{a}/dt=\mu\mathbf{E}(\mathbf{r},t), \tag{7}$$

where μ is the electron mobility. [The contribution of holes to Eq. (7) can be ignored because of the fast self-localization of holes which occurs in a time $\sim 10^{-14}$ s.] The field in the interaction region in Eq. (7) can be replaced with the field on the axis of this region. This does not affect the results obtained for times $t\ll\tau_e$ (τ_e is the screening time discussed below) and even if $t\sim\tau_e$, we can still obtain qualitative results. In fact, we shall ignore the screening-induced deformation of the Gaussian distribution of charges. Describing the equivalent electric circuit by the expression

$$U_0=u+RdQ/dt$$

and introducing a new variable

$$Q'=\frac{V_k}{V}S\rho_k\int_0^t\frac{da}{dt}\exp\left(-\frac{t}{\tau_r}\right)dt,$$

we finally obtain the following system of equations

$$\begin{aligned}\tau_e\frac{dQ'}{dt}&=\left(\frac{V_k}{V}Q-\frac{1}{2}\eta Q'\right)\exp\left(-\frac{t}{\tau_r}\right),\\ \tau_1\frac{dQ}{dt}&=Q_0+Q'-Q\end{aligned} \tag{8}$$

subject to the initial conditions $Q=Q_0$ and $Q'=0$ at $t=0$. Here, $Q_0=CU_0$, $\tau_1=RC$, $\tau_e=\varepsilon_0\varepsilon/\mu\rho_k$ ε is the permittivity of the medium, and ε_0 is the permittivity of vacuum. Subject to the condition $\tau_1\ll\tau_e$ satisfied in our experiments, Eq. (8) has the following asymptotic solution:

$$Q=Q'+Q_0,$$

$$Q'=\frac{2}{\eta'}\frac{V_k}{V}Q_0\left\{1-\exp\left[-\frac{\eta'}{2}\frac{\tau_r}{\tau_e}\left(1-\exp\left(-\frac{t}{\tau_r}\right)\right)\right]\right\},$$

where

$$\eta'=1-\frac{\pi^2}{3}\frac{r_k^2}{L^2}+\ldots\approx 1.$$

The current in this electric circuit is

$$J(t)\equiv\frac{dQ}{dt}=\frac{V_kQ_0}{V\tau_e}\exp\left(-\frac{t}{\tau_r}\right)\times\exp\left\{-\frac{\eta'}{2}\frac{\tau_r}{\tau_e}\left[1-\exp\left(-\frac{t}{\tau_r}\right)\right]\right\}.$$

The amplitude of the current is given by

$$J(0)=N_k(e\mu U_0/L^2).$$

In general, the amplitude of the photoconductivity signal voltage recorded by an oscilloscope can be represented by

$$U_{pc}=\alpha N_k\frac{e\mu U_0}{L^2}R\varphi\left(\frac{\tau_r}{\tau_x}\right). \tag{9}$$

Here, α is the geometric factor describing the deviation from the parallel-plate capacitor approximation ($\alpha=1$ applies in the approximations adopted above), $\varphi(\tau_r/\tau_x)$ is the function representing the transfer of the signal along the recording channel, and τ_x is the time constant of the transient characteristic of the recording channel.

Equation (9) was checked carefully against the experimental results. We determined the linearity of the signal as a function of the applied field U_0, the relation $U_{pc}\propto L^{-2}$, the proportionality of U_{pc} to the length of the interaction region l, and the dependence of the signal on the effective radius r_k [described by Eqs. (1) and (1′)].

The relationships (1) and (9) allow us to derive expressions for the ratios of the absorption coefficients β_2/β_3 and β_2/β_4. For a given value of U_{pc} and identical radii of the beams of the exciting radiation, they are

$$\frac{\beta_2}{\beta_3}=\frac{4\sqrt{2}}{9\sqrt{3}}\frac{\Omega_{\{2\}}}{\Omega_{\{3\}}}\frac{\tau_{\{3\}}}{\tau_{\{2\}}}\frac{I_{0\{3\}}^3}{I_{0\{2\}}^2}, \tag{10}$$

$$\frac{\beta_2}{\beta_4}=\frac{\sqrt{2}}{8}\frac{\Omega_{\{2\}}}{\Omega_{\{4\}}}\frac{\tau_{\{4\}}}{\tau_{\{2\}}}\frac{I_{0\{4\}}^4}{I_{0\{2\}}^2}. \tag{11}$$

The indices in braces in Eqs. (10) and (11) identify the parameters of the radiation resulting in, respectively, two-, three-, and four-photon excitation of nonequilibrium carriers. It should be mentioned that τ_r and μ are independent of the number of photons participating in the process and, con-

sequently, they do not occur in Eqs. (10) and (11), and this is true also of the geometric factor α.

EXPERIMENTAL RESULTS

Figures 2 and 3 show the experimental $U_{pc} = f(I_0)$ plots obtained for the investigated crystals. Each experimental point represents one measurement. All the measurements were carried out under identical conditions, i.e., the dimensions of the samples were the same ($L = 3$ mm, $l = 10$ mm), the cross section of the exciting beam reaching the entry surface of a crystal was the same for all the wavelengths, the voltage $U_0 = 3.6$ kV was the same, and the same recording apparatus ($\tau_x = 2$ ns) was employed. Clearly, the results are described satisfactorily by power laws (dashed lines) with exponents $K = 2$, 3, and 4 corresponding to the two-, three-, and four-photon excitation of nonequilibrium carriers. [We recall that the band gaps E_g of KCl, NaCl, KBr, and KI crystals are 8.7, 8.8, 7.3, and 6.4 eV (Ref. 13), and the energies of the photons representing the fourth, third, and second harmonics are 4.68, 3.51, and 2.37 eV].

It follows from Eqs. (10) and (11) and from Figs. 2 and 3 that the precision of the determination of the ratios of the multiphoton absorption coefficients β_2/β_3 and β_2/β_4 is governed essentially by the precision of determination of the spatial, temporal, and energy parameters of the exciting radiation. This was the reason for the stringent requirements that the quality of the laser pulses had to satisfy in our laser system. The results of measurements of these ratios are presented in Table I. The absolute values of the coefficients β_3 and β_4 were determined using the values of β_2 for a large number of wide-gap crystals,[4] which were determined at wavelengths $\lambda = 0.266$ and $0.355\ \mu$m (using the fourth and third harmonics of a picosecond YAG:Nd laser). The multiphoton absorption coefficients β_3 and β_4 found in this way for the investigated materials are also included in Table I. An analysis of the errors associated with the measurements of the energy and duration of the pulses, and of the beam radius (10, 20 and 15%, respectively) showed that after allowance for the scatter of the experimental points and the error in β_2 the multiphoton absorption coefficients differed from the values given above by a factor not exceeding 2.2 in the case of β_3 and not exceeding 2.8 in the case of β_4.

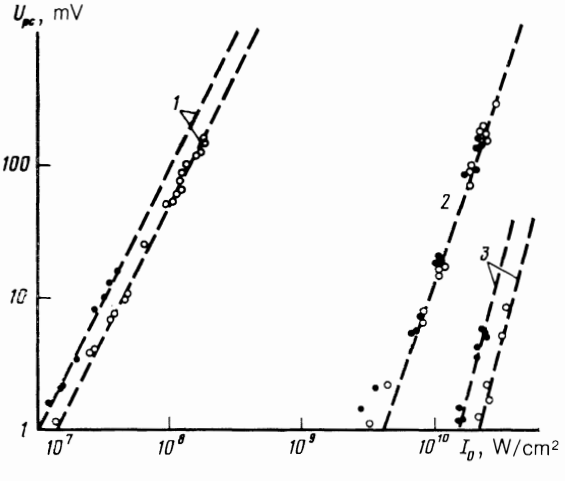

FIG. 2. Dependences of the photoconductivity signal U_{pc} on the density I_0 of the exciting radiation incident on KCl (○) and NaCl (●) crystals: 1) two-photon excitation ($\lambda = 0.266\ \mu$m); 2) three-photon excitation ($\lambda = 0.355\ \mu$m); 3) four-photon excitation ($\lambda = 0.532\ \mu$m). The density of nonequilibrium electrons was related to U_{pc} by $n_k = k \times 2.3 \times 10^{15} U_{pc}$ [cm^{-3}].

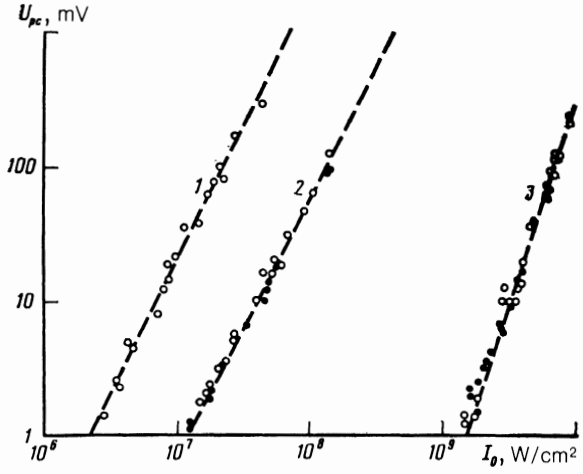

FIG. 3. Dependences of the photoconductivity signal U_{pc} on the intensity I_0 of the exciting radiation reaching KBr (○) and KI (●) crystals: 1) two-photon excitation of KBr ($\lambda = 0.266\ \mu$m); 2) two-photon excitation of KBr ($\lambda = 0.385\ \mu$m) and KI ($\lambda = 0.266\ \mu$m). The dependences of the photoconductivity signal for a KI crystal at the wavelengths $\lambda = 0.355$ and $0.266\ \mu$m coincide; 3) three-photon excitation ($\lambda = 0.532\ \mu$m). The density of nonequilibrium carriers was related to U_{pc} by $n_k = k \times 6.6 \times 10^{13}\ U_{pc}$ [cm^{-3}] for KBr and $n_k = k \times 4.2 \times 10^{15}\ U_{pc}$ [cm^{-3}] for KI.

We shall now compare the results obtained with the data of Refs. 5 and 6. The three-photon absorption cross section of KI reported in Ref. 5 was measured at the wavelength of $\lambda = 0.532\ \mu$m relative to the two-absorption at the wavelength $\lambda = 0.355\ \mu$m and it amounted to $\sigma_3 = 6 \times 10^{-81}$ cm$^6 \cdot$s^2, which (converted to the absorption coefficient) gave 4.9×10^{-22} cm$^3 \cdot$W^{-2}. The four-photon absorption cross section of NaCl ($\lambda = 0.532\ \mu$m) obtained in Ref. 6 was $\sigma_4 = 1.5 \times 10$ cm$^8 \cdot$s^3, corresponding to the absorption coefficient 0.65×10^{-36} cm$^5 \cdot$W^{-3}. Clearly, two sets of results agreed well for KI, but there was a considerable discrepancy in the case of NaCl. However, it should be noted that whereas in our case the error of the results was governed by the error in the determination of the parameters of the laser pulses and of the quantity β_2, in the case of photoacoustic measurements (and also in luminescence measurements) the results were affected additionally and significantly by the adopted model of the mechanism of energy transfer from nonequilibrium carriers (electrons) to the lattice; this—in the words of the authors of Ref. 6—could give rise to an error in σ_4 exceeding by more than one order of magnitude (in the direction of a larger value) the value given above.

The method used to find the ratios of the absorption coefficients allowed us to determine the spectral dependences of these coefficients $\beta_k(\lambda)$. In the two-photon absorption case we could obtain, by analogy with Eqs. (10) and (11), the following ratio.:

$$\frac{\beta_2(\lambda_0)}{\beta_2(\lambda)} = \frac{\lambda}{\lambda_0} \frac{\tau_{\{\lambda\}}}{\tau_{\{\lambda_0\}}} \frac{I^2_{0\{\lambda\}}}{I^2_{0\{\lambda_0\}}} \qquad (12)$$

and using a known value of $\beta_2(\lambda_0)$ we could determine

TABLE I.

	β_2, 10^{-9} cm·W^{-1} (Ref. 4) ($\lambda_{(2)}$, μm)	β_2/β_3, 10^{14} W·cm^{-2} ($\lambda_{(2)}$, $\lambda_{(3)}$, μm)	β_3, 10^{-24} cm^3·W^{-2} ($\lambda_{(2)}$, μm)	β_2/β_4, 10^{26} W·cm^{-4} ($\lambda_{(2)}$, $\lambda_{(4)}$, μm)
KCl	1.7 (0.266)	3.6 (0.266; 0.355)	4.7 (0.355)	9.3 (0.266; 0.532)
NaCl	3.5 (0.266)	5.3 (0.266; 0.355)	6.6 (0.355)	4.2 (0.266; 0.532)
KBr	2 (0.266)	7.6 (0.266; 0.532) 0.14 (0.355; 0.532)	2.6 (0.532)	–
KI	3.8 (0.266) 7.3 (0.355)	0.19 (0.266; 0.532) 0.17 (0.355; 0.532)	200 (0.532) 430 (0.532)	–

	β_4, 10^{-36} cm^5·W^{-3} ($\lambda_{(4)}$, μm)	$\beta_2(\lambda_0)/\beta_2(\lambda)$ (λ_0, λ, μm)	β_2, 10^{-9} cm·W^{-1} ($\lambda_{(2)}$, μm)	μ, cm^2·V^{-1}·s^{-1}
KCl	1.8 (0.532)	–	–	1.1
NaCl	8.3 (0.532)	–	–	1.0
KBr	–	55 (0.266; 0.355)	0.036 (0.355)	12
KI	–	1.1 (0.266; 0.355)	–	0.9

$\beta_2(\lambda)$ from the intensities $I_{0(\lambda)}$ and $I_{0(\lambda_0)}$ measured for a given value of U_{pc}. For example, in the case of the KBr crystal we could use the graphs of Fig. 3 to find the two-photon absorption coefficient at the wavelength $\lambda = 0.355\,\mu$m (Table I). A reduction in the coefficient β_2 at this wavelength by 1.5 orders of magnitude compared with its value at $\lambda = 0.266\,\mu$m was due to the fact that transitions of nonequilibrium carriers to the conduction band occurred in this case from the edge of the valence band. A similar result, i.e., a difference by two orders of magnitude between the photocurrent signals obtained as a result of one-photon excitation of carriers at wavelengths $\lambda = 0.133$ and $0.177\,\mu$m, was reported in Ref. 14. Table I gives our ratio of the absorption coefficients β_2 at the wavelengths $\lambda = 0.266$ and $0.385\,\mu$m for a crystal of KI. A comparison of the results obtained with the data of Ref. 4 demonstrated a satisfactory agreement (within the limits of the experimental error).

DETERMINATION OF THE DRIFT MOBILITY OF NONEQUILIBRIUM CARRIERS

Another possible application of the method of picosecond laser photoconductivity in studies of the properties of nonequilibrium carriers is determination of the drift mobilities of electrons in the conduction bands of wide-gap crystals. In fact, in the case of (for example) two-photon excitation of carriers for a known value of β_2 using Eqs. (1), (1′), and (9), we could determine the mobility μ from U_{pc} measured for a given intensity I_0. The resultant error was then mainly due to indeterminacy of the geometric factor α, which was known exactly only in the parallel-plate capacitor approximation. The signal transfer function $\varphi(\tau_r/\tau_x)$ could be obtained by the optical rectification method described above or by comparing the photoconductivity signals determined using oscilloscopes with different pass bands. These experiments demonstrated that in the investigated range of rates of excitation of nonequilibrium carriers, where the measured values of the electron recombination time τ_r were 1–6 ns, the signal transfer function could be described sufficiently accurately by a transient characteristic of an integrating circuit:

$$\varphi(\theta) = \exp\left(-\frac{1}{\theta-1}\ln\theta\right) = \begin{cases} 1, & \theta \to \infty \\ e^{-1}, & \theta = 1, \\ \theta, & \theta \to 0 \end{cases}$$

where $\theta = \tau_r/\tau_x$.

Using the data of Figs. 2 and 3 obtained for $\tau = 2$ ns, employing the value $\varphi(2/2) = 0.37$ for a KI crystal and $\varphi(5/2) = 0.54$ for the other crystals (in the case of a KI crystal under these excitation conditions we observed the shortest electron recombination times $\tau_r = 1$–2 ns), and assuming that $\alpha = 1$, we found the mobilities listed in Table I. The drift mobilities of electrons in KCl, NaCl, and KI crystals differed by more than one order of magnitude from the published Hall mobilities amounting to $(1–2)\times 10$ cm^2·V^{-1}·s^{-1} (Refs. 15 and 16). However, in the case of KBr the mobility μ found in this way was practically identical with the published Hall mobility. Such a large difference between the mobilities found by the method described above and those given in the literature cannot be explained by the indeterminacy of α. Moreover, the ratio of the drift mobilities in various crystals is independent of α and, for example, in the case of KBr and NaCl its value (for a fixed I_0) is given by

$$\frac{\mu_{KBr}}{\mu_{NaCl}} = \left(\frac{U_{pc}}{\beta_2\varphi}\right)_{KBr}\left(\frac{\beta_2\varphi}{U_{pc}}\right)_{NaCl} = 12.$$

A possible influence of the two-photon absorption coefficient on our results was checked by repeating the measurements of β_2 for KBr and NaCl crystals at $\lambda = 0.266\,\mu$m by a method described in Ref. 4. It was found that, within the limits of the experimental error, the values of β_2 were identical with those given in Ref. 4 (see Table I): $\beta_2 = 2.7\times 10^{-9}$ cm·W^{-1} for KBr and $\beta_2 = 3\times 10^{-9}$ cm·W^{-1} for NaCl. Hence, we assumed that an anomalously high (compared

with the other crystals) drift mobility of carriers did indeed occur in KBr. It should be pointed out also that our values of the mobilities were obtained for thermalized electrons and could not depend on the intensity of the exciting radiation, because the recorded signal was formed practically entirely after the end of a laser pulse.

IMPURITY PHOTOCONDUCTIVITY

The range of validity of the method of picosecond laser photoconductivity is not limited to the fundamental (interband) methods of excitation of nonequilibrium carriers. In view of the high sensitivity (the minimum detectable electron density in the conduction band is $\sim 10^{11}$–10^{12} cm^{-3}), this method may also be used to investigate impurity excitation and to determine the absorption cross sections or concentrations of electrically active impurities and defects in wide-gap crystals with very low linear (one-photon) absorption coefficients $\sim 10^{-5}$–10^{-6} cm^{-1}. The availability of several frequencies of the exciting radiation makes it possible to determine the position of the impurity levels in the band gap.

Excitation of nonequilibrium carriers as a result of impurity (extrinsic) absorption of light was investigated using KCl crystals with a considerable amount of OH^- and impurity. It was found that illumination of these samples at $\lambda = 0.388\ \mu$m not only resulted in interband excitation, but also in a strong impurity excitation of electrons to the conduction band, as demonstrated (curve 1 in Fig. 4) by the dependence of the photoconductivity signal with two characteristic regions: linear at low intensities (impurity excitation) and superlinear at higher intensities. The existence of a superlinear region could be easily understood by allowing in Eq. (9) for the simultaneous effects of three-photon (fundamental) and one-photon (impurity) absorption. In fact, in this case we should have

$$U_{pc} \propto \pi r_0^2 \left(\beta_1 I_0 + \frac{1}{9\sqrt{3}} \beta_3 I_0^3\right), \qquad (13)$$

where β_1 is the linear absorption coefficient, which amounted to 7×10^{-5} cm^{-1} when deduced from this experimental dependence. Substituting newly found β_1 and the value of β_2 measured earlier into Eq. (13), we obtained the intensity at which both terms in Eq. (13) became identical: $I_0' = 1.47\times 10^{10}$ W·cm^{-2}, in good agreement with the experimental results (Fig. 4). At intensities exceeding I_0' the dominant role was played by the three-photon absorption process. For example, already for $I_0 = 5\times 10^{10}$ W·cm^{-2} the second term in Eq. (13) was an order of magnitude greater than the first. In the case of excitation of nonequilibrium carriers in the same samples, but using radiations of different frequencies, it was found that the fourth harmonic gave rise to the usual quadratic dependence of the photoconductivity signal exactly as in the case of ultrapure crystals, whereas the second harmonic did cause impurity excitation, but its contribution was considerably less than in the case of excitation of carriers with the third-harmonic pulses.

A study of the temperature dependences of the photoconductivity signal revealed that KCl crystals having clearly an impurity photoconductivity at the wavelength $\lambda = 0.355$ μm underwent a major change of properties after the following thermal cycle: heating to a temperature T close to the melting point [$T = T_{mp} - (5$–$10)$°C, where

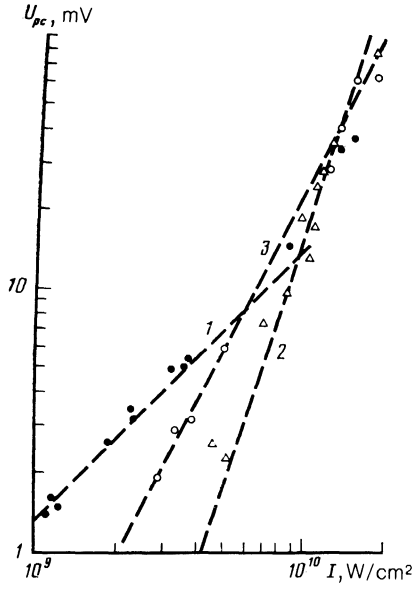

FIG. 4. Influence of heat treatment on the impurity component of the photoconductivity signal obtained from a CKl crystal. The points represent the experimental results and curves 1–3 are explained in the text.

$T_{mp} = 776$°C] → maintenance of this temperature for ≈ 30 min → fast cooling; it was then found that the dependence $U_{pc} = f(I_0)$ became practically cubic because of a reduction in the linear absorption coefficient by more than one order of magnitude. The value of the three-photon absorption coefficient then agreed (within the limits of the experimental error) with the value measured in the case of initially pure samples. The dependence obtained is plotted in Fig. 4 (curve 2). After heating of crystals to $T = T_{mp} - 100$ °C an intermediate situation was observed (curve 3 in Fig. 4).

This method of heat treatment of alkali halide crystals was used in Ref. 17 to study the laser damage thresholds of these materials when subjected to nanosecond pulses and the influence of the treatment on the photoconductivity (reduction of the signal after heat treatment in KBr crystals at the wavelength $\lambda = 0.355\ \mu$m) was reported in Ref. 11. It was established in Ref. 17 that samples with initially high thresholds were not subject to such a thermal interaction, although in the case of other crystals, which had initially lower strengths, the threshold increased considerably. For example, in the case of a KCl crystal at a wavelength of $\lambda = 1.064$ μm the threshold increased fivefold and it was practically identical with the thresholds of extremely strong samples. It was also found that heating to a temperature of 680 °C increased the threshold only slightly (by a factor of 1.5 in the case of KCl). Since in our case the initially pure samples were also unaffected by this heat treatment, we concluded that there was a correlation between an increase in the laser damage threshold in the nanosecond range and a reduction in the impurity component in the picosecond laser photoconductivity signal. We could also assume that a similar correlation was applied to the laser breakdown threshold in the picosecond range. We therefore carried out comparative measurements of the bulk damage threshold at the wavelengths of $\lambda = 1.064$ and 0.355 μm for initially pure and doped KCl crystals. The latter were investigated before and after the heat treatment described above (involving heating to 680° and 770 °C). The radiation incident on a crystal was

focused by a lens with $f = 45$ mm ($\lambda = 1.064$ μm) in the interior of a sample at a depth of 10 mm. The damage was observed visually under a microscope and it was manifested by the appearance of a spark. The threshold was assumed to be the intensity likely to cause damage with a probability of 50%. We thus established that, within the limits of the scatter of the experimental values, the laser damage thresholds of our crystals at these wavelengths did not change as a result of the heat treatment described above and remained equal to the thresholds determined for the initial pure samples. The heat treatment did have a significant influence on the nature of the dependence of the photoconductivity signal only in the case of excitation at the wavelength $\lambda = 0.355$ μm. At other wavelengths it had no effect at all ($\lambda = 0.266$ μm) or it did not alter significantly the results obtained before the heat treatment ($\lambda = 0.532$ μm).

The reported results of the investigation of the influence of heat treatment on the photoconductivity and breakdown thresholds could be used to draw the conclusion that in the case of laser damage to crystals by picosecond pulses the role of impurities (or inclusions) was clearly less important than in the case of damage by longer (for example, nanosecond) pulses.

CONCLUSIONS

Our investigation demonstrated that the method of picosecond laser photoconductivity is very effective in studies of electronic photoexcitation processes in wide-gap insulators. It can be used to detect reliably multiphoton processes, determine sufficiently accurately the corresponding absorption coefficients (using simple calibration against the known absorption), and find important characteristics of thermalized nonequilibrium electrons, such as their drift mobility. The high sensitivity of the method of picosecond laser photoconductivity makes it possible to detect very low concentrations of impurities in a crystal and to determine the ionization cross sections of these impurities and their depth.

The multiphoton absorption coefficients, carrier mobilities, and impurity photoconductivity determined in the present study are of interest in their own right in the physics of electronic processes in wide-gap insulators, and they also provide important information on the mechanisms of interaction of high-power laser pulses with wide-gap crystals resulting in laser damage.

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