Electro-optic and photorefractive properties of $\text{Bi}_4\text{Ge}_3\text{O}_{12}$ crystals in the ultraviolet spectral range

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For the first time to our knowledge, photorefractive effects have been observed in the ultraviolet spectral region in undoped crystals of $\text{Bi}_4\text{Ge}_3\text{O}_{12}$. For the investigation of the photorefractive properties we performed holographic experiments, and we further investigated fundamental properties, such as the photoconductivity and the dispersion of the electro-optic coefficients. Gain coefficients greatly exceeding the absorption losses and recording time constants $\approx 30\text{ ms}$ were observed in two-wave-mixing experiments with ultraviolet light in the $300$–$350$-nm spectral region at a $0.5\text{-W/cm}^2$ power level. The charge carriers primarily involved in charge transport are holes.

INTRODUCTION

The photorefractive effect arises under nonuniform illumination from a charge redistribution that causes a change in the crystal refractive index through the linear electro-optic effect. Because of potential applications of photorefractive materials in real-time holography, image processing, laser beam amplification, and optical phase conjugation, the interest in this field has grown considerably in the last few years. The main effort has been focused on materials that are photosensitive in the visible or near-infrared spectral range. Among this group of photorefractive materials, several ferroelectric crystals, such as $\text{LiNbO}_3$, $\text{BaTiO}_3$, and $\text{KNbO}_3$, and some photoconductive electro-optic crystals, such as $\text{Bi}_2\text{Ge}_2\text{O}_15$ and $\text{Bi}_2\text{SiO}_3$, are the best known to have good response in the visible spectral range. Semi-insulating semiconductor materials such as $\text{GaAs}$, $\text{GaAs:Cr}$, $\text{InP:Fe}$, and $\text{CdTe:In}$ have been shown to be photosensitive in the near infrared.

Until now, no systematic study of photorefraction in the ultraviolet (UV) spectral range has been undertaken to our knowledge. Photorefractive materials operating in the UV, however, could be useful for all types of coherent optical beam interactions, e.g., beam amplification, dynamical holography, phase conjugation, and photolithographic applications in which the use of shorter wavelengths leads to increased resolution. To the best of our knowledge, only preliminary studies of photorefractive effects in the UV have been reported, e.g., in $\text{KH}_2\text{PO}_4$ (Ref. 3) and $\text{RhZnBr}_4$ (Ref. 4) (both at low temperatures) and in $\text{LiNbO}_3$ (Refs. 5, 6) and $\text{LiTaO}_3$ (Ref. 7) in the near-UV spectral range.

The material used in this investigation for demonstrating photorefractive effects in the UV, $\text{Bi}_4\text{Ge}_3\text{O}_{12}$, belongs to the cubic point group $43m$. It is a well-known scintillator crystal for x-ray and positron detectors and can be grown with high quality and in large sizes. The material has a large transparency range of approximately $300$ nm to approximately $6\mu m$. In the visible spectral range, photorefractive effects recently have been observed in Cr-doped $\text{Bi}_4\text{Ge}_3\text{O}_{12}$ by Moya et al. as well as in Fe- and Mn-doped crystals by Kovacs et al. In the previous studies no photorefractive gratings could be recorded at visible wavelengths in undoped $\text{Bi}_4\text{Ge}_3\text{O}_{12}$ samples, which showed photoconductivity.

In this paper we report on the observation of photorefraction in undoped $\text{Bi}_4\text{Ge}_3\text{O}_{12}$ and present a detailed characterization of photoinduced refractive-index changes, photoconductivity, and dispersion of the electro-optic coefficients in the UV spectral range. To our knowledge, this is the first report of a photorefractive effect observed in an electro-optic crystal at a wavelength shorter than $350 \text{ nm}$ at room temperature. The electro-optic coefficients of $\text{Bi}_4\text{Ge}_3\text{O}_{12}$ measured in the spectral range of $305$–$633$ nm extend the previously determined values measured at approximately $405$–$630$ nm toward shorter wavelengths.

CRYSTAL PREPARATION AND FUNDAMENTAL PARAMETERS

The samples investigated in this study were rectangular parallelepipeds with dimensions of $4.88$ mm $\times 5.01$ mm $\times 5.26$ mm and faces perpendicular to the crystallographic $\langle 110 \rangle$, $\langle 110 \rangle$, and $\langle 001 \rangle$ axes. They were cut from a boule of pure $\text{Bi}_4\text{Ge}_3\text{O}_{12}$, the $\langle 110 \rangle$ faces were polished to optical quality with a planity of $\lambda/8$, and silver electrodes were painted on the $\langle 001 \rangle$ faces. Preliminary piezoelectric tests permitted the determination of the $\langle 110 \rangle$ and $\langle 110 \rangle$ directions in accordance with the standards on piezoelectric crystals.

$\text{Bi}_4\text{Ge}_3\text{O}_{12}$ is optically isotropic and is not optically active, and its refractive index has been determined by Bortfeld and Meier in the wavelength range of 407–644 nm. Throughout this work their single-term Sellmeier relation

$$n^2 - 1 = \frac{S_0 \lambda_0^2}{1 - (\lambda_0/\lambda)^2}$$

with $S_0 = 9.508 \times 10^{13}$ m$^{-2}$ and $\lambda_0 = 181.1$ nm will be used to fit our data. The refractive indices used in the UV are extrapolations from measurements in the visible; they have a larger uncertainty for $\lambda < 400$ nm ($\Delta n \approx 0.003$) than for $\lambda > 400$ nm ($\Delta n \approx 0.001$).
Absorption measurements in the wavelength region from 200 to 1000 nm were performed at room temperature with a Perkin-Elmer Model L9 spectrometer. The dispersion of light transmission in our undoped Bi₄Ge₃O₁₂ crystal is similar to the one reported in Ref. 12. There is no evidence for an absorption band between the lattice absorption located at λ ≈ 6 μm and the electronic absorption edge, which is near λ ≈ 300 nm. The absorption constant α can be calculated from the measured transmission of incoherent light if multiple reflections at the crystal surfaces are taken into account. At the lower wavelength used for the photorefractive experiments we calculated α(334 nm) = (0.13 ± 0.03) cm⁻¹. Table 1 summarizes the measured refractive indices, dielectric constant, absorption, and other physical properties of Bi₄Ge₃O₁₂ crystals.

**ELECTRO-OPTIC AND POLARIZATION-OPTIC COEFFICIENTS**

Because no detailed investigation of the dispersion and size of the electro-optic coefficients in the UV spectral range has yet been reported to our knowledge, we investigated this parameter first. Because of its point-group symmetry, Bi₄Ge₃O₁₂ possesses only three nonvanishing (and equal) electro-optic coefficients, \( r_{41} = r_{52} = r_{63} \neq 0 \), which describe changes of the optical indicatrix resulting from an applied electric field. In a coordinate system with \( x_1 || [100], x_2 || [010], x_3 || [001] \), and a field direction parallel to \( x_3 \) we simply have

\[
\Delta \left( \frac{1}{n^2} \right)_{12} = r_{63} E_3 = r_{41} E_3. \tag{2}
\]

If the field-induced crystal polarization \( P \), instead of the electric field, is chosen as the driving term, Eq. (2) is replaced by

\[
\Delta \left( \frac{1}{n^2} \right)_{12} = f_{41} P_3, \tag{3}
\]

where \( f_{41} \) is an element of the optical polarization tensor \( f \), which submits the same symmetry constraints as does the \( r \) tensor. In particular, for the point group 43m the only nonvanishing elements of \( r \) and \( f \) are simply related by \( f_{41} = r_{41}(\varepsilon_0(\varepsilon - 1))^{-1} \) (Table 1). Element \( r_{41} \) was measured by the modulated-field method with a 10-kHz ac electric field applied in the [001] direction. A polarizer placed in front of the crystal and an analyzer placed behind the crystal were oriented at ±45° with respect to the crystal [110] axis. The resulting modulated intensity of the light traveling parallel to [110] were detected by an RCA 1P28 photomultiplier tube. For this geometric configuration the electric-field-induced phase shift between a wave polarized along the [001] axis and a wave polarized along the [110] axis is \( \Delta \phi = (2\pi\lambda)/(n^2/2 r_{41} E_3) d \), where \( d \) is the crystal thickness. The reduced half-wave voltage \( v_w \) and the electro-optic coefficient \( r_{41} \) are then related by \( v_w = \lambda/(n r_{41}) \).

Measured values of \( v_w \) and \( r_{41} \) in the wavelength range 300–700 nm are shown in Fig. 1 and listed in Table 2. Although \( v_w \) has a minimum at \( \lambda = 360 \) nm, \( r_{41} \) monotonically decreases toward shorter wavelengths. An extrapolation of the measured dispersion of the electro-optic coefficients shows that \( r_{41} = 0 \) at \( \lambda \approx 260 \) nm, which is in the region of maximum absorption. The straight lines in Fig. 1 are best fits to the data; the best fits were computed

![Figure 1](image_url)
by following the polarization-potential model of Wemple and DiDomenico. This model takes into consideration the crystal-polarization-induced shift of the optical absorption edge and the related change of the Sellmeier oscillator frequencies and strengths. Differentiating the refractive-index dispersion of Eq. (1) with respect to the field-induced crystal polarization $P$ yields the following dispersion relation for the electro-optic coefficient $r(\lambda)$ (Ref. 16):

$$r(\lambda) = \varepsilon_0 (\epsilon - 1) \left( \frac{1}{n^2(\lambda)} - 1 \right) \frac{\partial \lambda_0}{\partial P} \left( \frac{\lambda_0}{\lambda} \right)^2 \times \left[ (1 - K) + (1 + K) \left( \frac{\lambda_0}{\lambda} \right)^2 \right].$$

(4)

In Eq. (4), $\lambda_0$ and $S_0$ are the oscillator wavelength and the oscillator strength, respectively, in the Sellmeier relation given by Eq. (1); $\varepsilon$ is the static dielectric constant, $\partial \lambda_0/\partial P$ represents the polarization-induced shift of the resonance wavelength $\lambda_0$, and $K$ is the dispersion constant, defined by

$$K = -\frac{\partial (S_0 \lambda_0)}{\partial P} \frac{\partial \lambda_0}{\partial P}.$$  

(5)

Equation (4) predicts a linear relationship between $r(1 - 1/n^2)^{-2}$ and $(\lambda_0/\lambda)^2$, which is well fulfilled in the case of Bi$_4$Ge$_3$O$_{12}$ (Fig. 2). From a least-squares fit of $r(\lambda)$, one obtains for the dispersion constant $K = 2.8 \pm 0.2$, and for the polarization-induced shift of the resonance wavelength $\partial \lambda_0/\partial P = (4.7 \pm 0.4) \times 10^{-9}$ m$^2$/C. This corresponds to $\partial E_p/\partial P = 0.18 \pm 0.02$ eV m$^2$/C, where $E_p = h\omega/\lambda_0$ is the oscillator energy. In the literature, no information could be found about the absolute sign of the electro-optic coefficient in Bi$_4$Ge$_3$O$_{12}$. Knowing the precise orientation and direction of crystallographic axes, the latter being determined by piezoelectric tests (piezoelectric coefficient $d_{33} > 0$), and considering the experimentally observed relative phase between the applied electric field and the transmitted and modulated light intensities, we conclude that the sign of the electro-optic coefficient $r_{41}$ is positive.

###暗电流和光电导

导电性是一个物理性质，它强烈影响了光非线性材料的性能。为了这个原因，我们进行了暗电导和光电导的详细研究，它们是由表

<table>
<thead>
<tr>
<th>$\lambda$ (nm)</th>
<th>$n$</th>
<th>$r_{41}$ (pm/V) (±0.02)</th>
<th>$n^2r$ (pm/V)</th>
<th>$\nu_\omega = \lambda/(n^2\nu)$ (kV)</th>
<th>$\sigma_{ph}$ [(\Omega)-cm]$^{-1}$]</th>
<th>$\phi_\mu \tau$ (10$^{-10}$ cm$^2$/V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>632.8</td>
<td>2.097</td>
<td>+0.96</td>
<td>8.9</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>514.5</td>
<td>2.135</td>
<td>+0.69</td>
<td>8.7</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>488.9</td>
<td>2.148</td>
<td>+0.86</td>
<td>8.5</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>457.9</td>
<td>2.167</td>
<td>+0.83</td>
<td>8.4</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>363.9</td>
<td>2.265</td>
<td>+0.62</td>
<td>7.2</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>351.1</td>
<td>2.291</td>
<td>+0.57</td>
<td>6.9</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>334.5</td>
<td>2.326</td>
<td>+0.49</td>
<td>6.2</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>305.4</td>
<td>2.410</td>
<td>+0.33</td>
<td>4.6</td>
<td></td>
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<td></td>
</tr>
</tbody>
</table>

* For $I = 1$ W/cm$^2$.

Table 2. 电光和光电导热学性质的Bi$_4$Ge$_3$O$_{12}$

通过观测光电导值，我们检测到暗电导和光电导的特性，它们是由表

**图2** 暗电导和光电导的线性关系图。对于Bi$_4$Ge$_3$O$_{12}$晶体

**图3** 光强与电导的线性关系图。入射：电场强度$E_p$为4 kV/cm。
ductivity at room temperature is \( \sigma_d = 5.2 \times 10^{-14} (\Omega \text{ cm})^{-1} \). In the temperature range of 90–200°C, the dark conductivity follows an exponential law of the type \( \sigma_d = \sigma_0 \exp(-\Delta E/k_BT) \) with an activation energy \( \Delta E = 0.90 \pm 0.06 \text{ eV} \). As is shown in Fig. 3, the photoconductivity \( \sigma_{ph} \) increases linearly with intensity at all wavelengths. It is given to a first approximation by

\[
\sigma_{ph} = e \alpha I (\phi \mu \tau),
\]

where \( e \) is the elementary charge, \( \alpha \) is the optical absorption constant, \( I \) is the light intensity, \( h \nu \) is the photon energy, \( \phi \) is the quantum efficiency for generating a free charge carrier per absorbed photon, \( \mu \) is the average carrier mobility, and \( \tau \) is the lifetime of a free charge carrier before recombination in a deep trap. Note that in Eq. (6) it was assumed that only one kind of charge carrier (either electrons or holes) contributes to the photoconduction. Although the product \( \mu \tau \) is expected to be wavelength independent, \( \phi \) (and thus \( \phi \mu \tau \)) depends on the photon energy (Table 2) and increases toward the absorption edge.

The values measured in this work, e.g., \( \phi \mu \tau (\lambda = 351 \text{ nm}) = (5 \pm 0.7) \times 10^{-10} \text{ cm}^2/\text{V} \) are comparable with \( \phi \mu \tau (\lambda = 355 \text{ nm}) = 3 \times 10^{-10} \text{ cm}^2/\text{V} \) measured in undoped crystals with spectral lamps. On the contrary, the values reported in Ref. 9 for undoped crystals were \( \sim 2 \) orders of magnitude larger, probably because the crystals used in Ref. 9 had a smaller density of traps.

From the results of photorefractive experiments (see the next section) we determined the mobility–lifetime product \( \mu \tau = (1.5 \pm 0.4) \times 10^{-10} \text{ cm}^2/\text{V} \). By using this value we estimated the value of the quantum efficiency \( \phi \). For the shorter wavelength used (334.5 nm) we obtained \( \phi = 0.13 \pm 0.04 \).

### PHOTOINDUCED REFRACTIVE-INDEX CHANGES AND TWO-WAVE-MIXING EXPERIMENTS

#### Theory

The first complete theoretical description of the photorefractive effect was given by Kukhtarev et al.\(^{17}\) We summarize some of their results, which will be used below to describe our measurements.

If photovoltaic effects are neglected, the first-order component of the steady-state space-charge field \( E_{sc} \) created by a sinusoidal light distribution is given by

\[
E_{sc} = -m' \frac{E_s^2 E_0}{(E_s + E_D)^2 + E_0^2} - \frac{im}{2} \frac{E_s^2 E_D + E_s E_0^2 + E_s E_D E_0}{(E_s + E_D)^2 + E_0^2},
\]

where the real part is a component in phase with the illuminating light fringes and the imaginary part is the \( \pi/2 \)-phase-shifted component. In Eq. (7) \( m' \) is the effective modulation index of the light fringes and \( E_0 \) is the applied field;

\[
E_D = \frac{q k_B T 2\pi}{e B \Lambda}
\]

is the diffusion field at temperature \( T \), where \( k_B \) is the Boltzmann constant, \( q \) is the charge-carrier charge, which is equal to \(+e\) (the elementary charge) for hole conductivity and to \(-e\) for electron conductivity, and \( \Lambda \) is the grating spacing. The limiting field \( E_L \) is given by

\[
E_L = \frac{q \Lambda}{\varepsilon_0 2\pi N_{eff}},
\]

where \( \varepsilon \) is the relative dielectric constant and \( \varepsilon_0 \) is the permittivity of vacuum. The factor \( N_{eff} \) represents an effective density of traps given by \( N_{eff} = N_D (N_D - N_A)/N_P \), where \( N_D \) is the donor density and \( N_A \) is the trap density in the crystal.

The effective index change \( \Delta n \) is proportional to the absolute value of the space-charge field \( |E_{sc}| \). For small values of \( \Delta n \) the diffraction efficiency measured in Bragg-diffraction experiments depends quadratically on \( \Delta n \) and thus on \( |E_{sc}| \). For large grating spacings (small \( E_{sc} \), large \( E_0 \)), \( |E_{sc}| \) depends linearly on the applied field \( E_0 \), which leads one therefore to expect a quadratic increase of the diffraction efficiency with \( E_0 \).

The imaginary part of the space-charge field \( E_{ic} \) in Eq. (7) is responsible for the net energy transfer between the pump and the signal waves in two-beam-coupling experiments. This permits the use of photorefractive materials for laser beam and image amplification. The signal beam amplification in the crystal is described by \( I_s(d) = I_s(0) \exp((\Gamma - \alpha)d) \), where \( d \) is the crystal thickness. The exponential gain \( \Gamma \) is related to the photorefractive parameters of the crystal. For \( \text{Bi}_4\text{Ge}_3\text{O}_{12} \) in the configuration shown in Fig. 4 it is given by\(^{17}\)

\[
\Gamma = \frac{2\pi n^3 r_{44} E_D^2 E_0^2 + E_D^2 E_s + E_D E_0^2}{\lambda \cos \theta (E_s + E_0)^2 + E_0^2},
\]

where \( 2\theta \) is the angle between the two recording beams in the crystal and \( \lambda \) is the vacuum wavelength.

In the simplest approximation, the dynamics of the grating buildup, grating erase with one homogeneous UV erase beam, and grating decay in the dark can be de-
scribed by simple exponential laws. The recording process is given by

$$\Delta n(t) = \Delta n_0[1 - \exp(-t/\tau_{\text{writing}})]$$  \hspace{1cm} (11)

where $\Delta n$ represents the refractive-index change. The dark decay and erasure are described by

$$\Delta n(t) = \Delta n_0 \exp(-t/\tau_\text{2})$$  \hspace{1cm} (12)

where $\tau_\text{2}$ is the respective time constant. The theory predicts the following dependence of the recording and erasure times of the space-charge field on the grating spacing $\Lambda$:

$$\tau = \tau_{\text{die}} \left[ 1 + \frac{K^2}{K_0^2} \right]^{-1/2} \left[ 1 + \frac{K_0^2}{K^2} \right]^{-1/2}$$

where $K = 2\pi/\Lambda$ is the grating wave vector and $\tau_{\text{die}}$ is the dielectric relaxation time. In Eq. (13)

$$K_0^2 = \frac{\varepsilon \gamma N_A}{\mu k_B T} = \frac{e}{\varepsilon_0 k_B T \mu \tau}$$

where $\gamma$ is the recombination constant, $N_A$ is the density of traps in the crystal, and $\mu$ is the mobility. The Debye wave vector $K_0$ is given by

$$K_0^2 = \frac{\varepsilon^2 N_{\text{eff}}}{\varepsilon_0 k_B T}$$

Because $N_{\text{eff}}$ can be determined independently by two-beam-coupling investigations (see above), a measurement of $\tau(\Lambda)$ gives direct information on $K_0$ and thus on the product $\mu \tau$. It follows from Eq. (13) that, if $K < K_0$, the response is faster at large grating spacings. The contrary is true for $K_0 < K_0$.

Experiments

The holographic investigations of the photorefractive effect in Bi$_4$Ge$_3$O$_{12}$ were performed by employing the geometry shown in Fig. 4. In this arrangement the beams diffracted by the phase grating conserve the polarization of the incident beams, and energy transfer between the two recording beams (beam coupling) can be investigated. The signal beam $I_s$ and the pump beam $I_p$ for recording the refractive index gratings were from a Spectra-Physics Ar$^+$-ion laser operating in the mid-UV region. The multiline laser radiation was separated outside the cavity, and the laser line at either $\lambda = 351.1$ or $\lambda = 334.5$ nm was used for the investigation of photorefractive gratings. For Bragg-diffraction experiments a weak He–Ne laser beam ($\lambda = 632.8$ nm) was used as the probe beam. The diffraction efficiency $\eta$ of the hologram, which is defined as the ratio of the diffracted wave intensity to the incident wave intensity, was monitored by detecting the diffracted He–Ne beam with a photomultiplier tube (RCA 1P28). For the measurements with an applied external dc field, the field was always in the positive [001] direction.

From the results of the Bragg-diffraction experiments we characterized the time dependence of the photorefractive grating buildup and decay and the magnitude of the refractive-index changes. In the samples that we investigated, the time dependence of the refractive-index changes could be satisfactorily described by the simple exponential laws of Eqs. (11) and (12) (Fig. 5). Previous investigations of doped Bi$_4$Ge$_3$O$_{12}$ crystals, were performed by employing the ge-

![Fig. 5. Photorefractive recording—erasure cycle at wavelength $\lambda = 351$ nm. Experimental conditions: grating spacing $A = 1.94 \mu m$; recording intensity $17$ mW/cm$^2$; erasure intensity $11$ mW/cm$^2$; no externally applied electric field. The solid curves represent simple exponential fits to the data.](image-url)

![Fig. 6. Recording times (filled symbols) and erasure times (open symbols) of the photorefractive gratings in Bi$_4$Ge$_3$O$_{12}$ measured by Bragg diffraction. Squares: $\lambda = 351.1$ nm, $A = 2.5$ $\mu m$, $E_0 = 0$; circles: $\lambda = 334.5$ nm, $A = 0.8$ $\mu m$, $E_0 = 0$.](image-url)
lar to the one just described were previously observed in Bi$_{12}$SiO$_{20}$ crystals and KNBO$_3$ crystals. They have been ascribed to a light-intensity-dependent population of shallow traps in the crystals. However, in both of these crystals, besides the strong dependence on the history of the sample, the dark decays also showed a pronounced nonexponential time dependence. In addition, the presence of a large number of shallow traps should probably also result in a nonlinear dependence of the photoconductivity on the illuminating light intensity. As may be seen from Fig. 3, this is not the case for our Bi$_4$Ge$_3$O$_{12}$ crystals. We therefore believe that in our case the reason for the observed dependence of the dark decay on the sample history could be different from the one reported in Ref. 18.

Because we found a linear dependence of the photoconductivity on the light intensity, we expected the time constant for recording and erasure to be inversely proportional to the illuminating power density ($\tau \propto 1/I$). This is verified by the unity slopes of the straight lines shown in Fig. 6. A recording time constant of $\tau = 60$ ms is predicted for $I = 1$ W/cm$^2$ at $\lambda = 351$ nm by extrapolating the straight lines of Fig. 6 to higher intensities. By using recording beams with shorter wavelengths (e.g., $\lambda = 334$ nm) this time constant can be further decreased. For $\lambda = 334$ nm and $I = 1$ W/cm$^2$ we obtained $\tau = 14$ ms. Furthermore, in the 310-nm region, in which powerful excimer lasers, such as XeCl ($\lambda = 308$ nm), are available, the photoconductivity is expected to increase by more than 1 order of magnitude with respect to that at $\lambda = 334$ nm. By using such a wavelength at the same power levels, one can expect recording times shorter than 1 ms. It should be mentioned that a photorefractive grating can also be recorded in our crystals by using visible wavelengths. However, the grating buildup time at, e.g., $\lambda = 514$ nm is larger by approximately 2 orders of magnitude than the one observed in the UV at the same power levels.

The measured angle dependence of the response time for recording at $\lambda = 334$ nm with an intensity $I = 34$ mW/cm$^2$ is shown in Fig. 7. The solid curve in the figure is the best fit to Eq. (13) with a fixed value of $K_0$ obtained by inserting the value of $N_{eff}$ (derived below from two-beam-coupling measurements, Fig. 9) into Eq. (15). In this way we find $K_0^2 = (2.56 \pm 0.7) \times 10^{13}$ m$^{-2}$, which implies $\mu \tau = (1.5 \pm 0.4) \times 10^{-4}$ cm$^2$/V. This result indicates that in Bi$_4$Ge$_3$O$_{12}$, as in the fastest-responding photorefractive materials, such as KNBO$_3$ and Bi$_{12}$SiO$_{20}$, the drift length $L_D = \mu \tau E_0$ of the free charges can reach values comparable with the fringe spacing. For example, for an applied field of 10 kV/cm the drift length is 1.5 $\mu$m.

As expected, for large grating spacings the steady-state diffraction efficiency $\eta$ depends quadratically on the externally applied field $E_0$. This is shown in Fig. 8 for recording with a grating spacing $\Delta = 9$ $\mu$m. The diffraction efficiency observed in our samples reached a value of approximately 1%/cm, which corresponds to a refractive-index change of approximately $2 \times 10^{-6}$. This is less than is normally obtained in most ferroelectric photorefractive crystals, such as BaTiO$_3$, KNBO$_3$, and LiNbO$_3$. However, because large, low-cost crystals of Bi$_4$Ge$_3$O$_{12}$ can be grown, the small refractive-index changes are not a fundamental obstacle to the use of this crystal for dynamic holography.

Measuring the energy transfer between the pump and the signal waves in a two-wave-mixing configuration gave information about both the sign of the majority charge carriers and the density of traps $N_A$ in the crystal. For this purpose we slightly modified the setup shown in Fig. 4 by inserting a neutral-density filter in front of the crystal to attenuate the signal beam by a factor of 300. The intensity of this beam after it passed the crystal sample was detected by another photomultiplier tube. Figure 9 shows...
the exponential gain $\Gamma$ as a function of the grating spacing $\Lambda$ for two different values of $E_0$. These measurements can be used to obtain an approximate value for the effective trap density $N_{eff}$. A fit to the experimental data using Eq. (10) gives $N_{eff} = 2.1 \times 10^{18}$ cm$^{-3}$ (Fig. 9). In Eq. (10) the signs of both $E_0$ and $E_0$ depend on the sign of the charge $q$. Therefore the second factor in Eq. (10) is positive if hole conductivity predominates and negative if electron conductivity predominates. Because the first factor is positive ($\xi_0 > 0$) and the experimentally observed exponential gain $\Gamma$ is also positive, holes are the majority charge carriers responsible for the buildup of the space-charge field in our Bi$_4$Ge$_2$O$_{12}$ crystals. It should further be noted that the observed exponential gains $\Gamma$ (Fig. 9) exceed by as much as a factor of 4 the absorption coefficient $\alpha = 0.06$ cm$^{-1}$ at the recording wavelength of $\lambda = 351$ nm. Effective amplification factors $\exp[H(\Gamma - \alpha)d]$ larger than unity are therefore possible, and it is meaningful to propose the use of Bi$_4$Ge$_2$O$_{12}$ crystals for laser beam amplification in the UV spectral range.

The photorefractive sensitivity at the initial stage of the recording process is a useful parameter for describing the photorefractive characteristics of a material. We alternatively define this photosensitivity to be $S_{\alpha} = d(\Delta n)/d(\alpha d)$, the refractive-index change per unit absorbed energy and volume, and $S_a = d(\Delta n)/d(E_0)$, the refractive-index change per unit incident energy and volume. Typical values of $(0.05-0.1) \times 10^{-3}$ cm$^2$J$/S_{\beta}$ and $(2.5\rightarrow 5) \times 10^{-6}$ cm$^2$/J$/S_a$ were measured at $\lambda = 351$ nm without an applied field. Values larger by as much as a factor of 5 can be obtained by using shorter wavelengths or by applying an external electric field. The photorefractive sensitivities determined for Bi$_4$Ge$_2$O$_{12}$ are approximately 2 orders of magnitude smaller than, e.g., those in KNbO$_3$ crystals because electro-optic coefficients ($r_{41} = 0.57$ pm/V at $\lambda = 351$ nm) are approximately 2 orders of magnitude smaller than those in KNbO$_3$.

Because the wavelengths of operation of our Bi$_4$Ge$_2$O$_{12}$ crystal are relatively close to the absorption edge, we investigated whether band-edge effects, such as the Franz-Keldysh effect, contribute to the generation of the refractive-index gratings. However, the results of investigations made for different crystal orientations and for different values of the applied electric field indicate that such effects are negligible in Bi$_4$Ge$_2$O$_{12}$ crystals at all wavelengths longer than 330 nm. At such wavelengths the contribution of the Franz-Keldysh effect to the refractive index gratings would not exceed $\Delta n = 10^{-4}$ for recording with an applied field of 10 kV/cm.

CONCLUSIONS

In summary, we have observed, for the first time to our knowledge, photorefractive effects in the UV spectral range by using undoped Bi$_4$Ge$_2$O$_{12}$ crystals. Experiments were performed to characterize material parameters relevant to the photorefractive effect and to investigate the dynamics of volume-phase hologram formation in this crystal. Because large crystals of Bi$_4$Ge$_2$O$_{12}$ can be grown easily, the disadvantage of relatively small electro-optic coefficients can be partly compensated for by using longer crystals. In fact, in our two-beam-coupling experiments effective amplification factors $\exp[H(\Gamma - \alpha)d]$ larger than unity have been observed in 0.49-cm-long crystals. This material therefore seems attractive for coherent image amplification, optical phase conjugation, and other nonlinear-optical applications in the UV spectral range. In addition, Bi$_4$Ge$_2$O$_{12}$ crystals belong to a group of materials having fast recording times and could thus find applications in dynamic holography using ultraviolet lasers, including XeCl, N$_2$, and XeF excimer lasers. This is especially the case if the recording wavelength is in the region of 310–330 nm, for which the extrapolated recording times for optical power densities of 1 W/cm$^2$ are only a few milliseconds. However, better material performance could probably be attained in reduced crystals showing enhanced photoconductivities. Further investigations of suitable reduction methods are planned.

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REFERENCES


