Femtosecond crystallographic experiment in wide-bandgap LiF crystal

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Abstract: We report a femtosecond crystallographic study of the dependence of the free-carries generation to the alignment of a crystalline sample to the laser polarization. The probe pulse transmission exhibits a π/2 modulation that is shown to be correlated with the direction dependence of the effective electron mass. This observation suggests that nonlinear ionization is the first channel for free electron generation during the laser pulse. Moreover, the temporal evolution of the probe pulse transmission indicates the dominance of the avalanche ionization and that nonlinear ionization provides the initial seed electrons for avalanche.

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OCIS codes: (190.4180) Multiphoton processes; (320.7110) Ultrafast nonlinear optics.

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1. Introduction

Nonlinear absorption of the photons in wide band-gap dielectric materials by high-intensity ultrashort pulse has been an area of intense research during the last decades. Many different nonlinear ionization processes have been proposed to explain the generation of free electronic carriers: multiphoton ionization [1], tunnel ionization [2], and avalanche ionization [3,4]. Whether multiphoton ionization is solely responsible for the free carrier generation, or whether avalanche plays a role, is still the subject of active research and debate. For relatively longer pulse duration (>100 fs) avalanche ionization is expected to dominate laser dielectric interactions [2], because there is sufficient time for inverse bremsstrahlung and impact ionization to produce enough electrons with kinetic energy above the band gap of the material. For short pulse (< 100 fs), however, it is suggested that multiphoton ionization is the important mechanism responsible for the free-electron generation [5], and that avalanche plays no role. Avalanche ionization requires lower intensities than multiphoton ionization but it also requires time to build up. Experimentally it may be difficult to identify the individual processes, because free-electron generation can result from a complex interplay between avalanche, multiphoton and tunnel ionization [6].

Past time-resolved interferometric measurements investigating the dynamics of laser-generated free carriers in dielectrics have suggested that multiphoton ionization is the dominant ionization mechanism with $k = 6$ in SiO$_2$, Al$_2$O$_3$, and $k = 5$ in MgO [7]. In this case the free carrier density is given by the following relation: $\rho(I) \sim I^k$, where $k$ is the multiphoton order and $I(t)$ is the intensity of the laser pulse. These estimations were later confirmed by polarisation dependent measurements of free carrier concentration in dielectrics generated by short pulse (~50 fs) [8]. In this experiment, the rate of multiphoton ionization was found to be significantly higher for linear polarization than for circular. On the other hand, polarisation dependent experiments with pulses of 0.8 ps duration showed that the ionization rates are independent of the polarization and that avalanche ionization should be dominant for longer pulses [9]. In contradiction to that, many different works have explained free carrier generation in dielectric material in terms of a combined avalanche-multiphoton ionization process [6,10]. In this case the electron density evolution is described with a simple rate equation:

$$\frac{dn}{dt} = \alpha I(t)n(t) + \sigma_k I^k; \quad (1)$$

where $\alpha$ is the avalanche coefficient, and $\sigma_k$ is the $k$-photon absorption cross section. Recently, Rajeev et al. [10] introduced a field-assisted avalanche model (cold avalanche ionization) for the explanation of the observation of avalanche signatures for pulses below 100 fs. More recently Deng et al. [11] have presented theoretical evidence for the cold avalanche ionization during carries generation in dielectrics.

In this article, we report time-resolved interferometric measurements investigating the dynamics of laser-generated free carriers in dielectrics have suggested that multiphoton ionization is the dominant ionization mechanism with $k = 6$ in SiO$_2$, Al$_2$O$_3$, and $k = 5$ in MgO [7]. In this case the free carrier density is given by the following relation: $\rho(I) \sim I^k$, where $k$ is the multiphoton order and $I(t)$ is the intensity of the laser pulse. These estimations were later confirmed by polarisation dependent measurements of free carrier concentration in dielectrics generated by short pulse (~50 fs) [8]. In this experiment, the rate of multiphoton ionization was found to be significantly higher for linear polarization than for circular. On the other hand, polarisation dependent experiments with pulses of 0.8 ps duration showed that the ionization rates are independent of the polarization and that avalanche ionization should be dominant for longer pulses [9]. In contradiction to that, many different works have explained free carrier generation in dielectric material in terms of a combined avalanche-multiphoton ionization process [6,10]. In this case the electron density evolution is described with a simple rate equation:

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In this article, we report time-resolved studies of the dependence of the transmitted light on the alignment of the crystal with respect to the laser polarization direction. A 266 nm UV pulse used to probe the refractive index changes induced in the crystal by an intense IR pump pulse (Fig. 1). We found that the ionization rates are maximized when the polarization of the IR field is aligned with the lattice axis, this indicates that the multiphoton ionization rate depends on the alignment of the lattice. Nevertheless, the strong modulation implies that multiphoton ionization by valence electrons is the first channel for free electron generation during the laser pulse. Measurement of the temporal evolution of the transmission revealed that avalanche ionization is the dominant excitation mechanism, the multiphoton absorption only providing the seed electrons for this avalanche process. In this scenario, the seed
electrons are produced by multiphoton ionization at the peak of the pulse, after which an avalanche produces a critical density.

Gertsvolf et al. [12] have performed similar experiments by measuring the intensity of the transmitted pump pulse. The principal difference between their work and our experiment is that we used a combination of short IR pulses to excite the sample, and UV pulse to probe the properties of the ionization. This difference is important because the propagation of an intense ultrashort pulse through a transparent medium is usually accompanied by many different nonlinear effects, such as self nonlinear absorption, catastrophic collapse etc. In addition, angle dependent absorption in centrosymmetric crystals was already observed in many different works [13].

2. Mathematical description

2.1 Strong-electric-field interband transitions

Multiphoton ionization and tunnel ionization are effects of a strong electric field. Both processes shift electrons from the valence band to the conduction band with help of the electric laser field. The photoionization process is sensitive to the Keldysh parameter [2,14]:

$$\gamma = \frac{\omega \sqrt{m_{\text{red}} \Delta}}{eE_L}, \quad (2)$$

where $\Delta$ is the bandgap, $\omega$ and $E_L$ the frequency and amplitude of electric laser field and $m_{\text{red}}$ is the reduced effective mass.

In the case of extremely high electric fields and low laser frequencies ($\gamma \ll 1$), tunneling through the binding barrier takes place during a time shorter than a laser period. Under these conditions, the ionization rate can be described by

$$z = \frac{2}{9\pi^2} \frac{\Delta (m_{\text{red}} \Delta)^{3/2}}{\hbar^2 (\omega \Delta)^{3/2}} \times \exp \left\{ -\frac{\pi \Delta \gamma}{2 \hbar \omega} \left( 1 - \frac{\gamma^2}{8} \right) \right\}. \quad (3)$$

For comparably low electric fields and high laser frequencies ($\gamma \gg 1$), the case of multiphoton ionization is given, and the ionization rate can be approximated by

$$\sigma_k = \frac{2\omega (m_{\text{red}} \omega)}{9\pi^2} \frac{2}{\hbar} \left( 1 + \frac{\hbar^2}{2m_{\text{red}} \omega} \frac{\Delta^2}{\hbar^2} \right) \times \phi \left( \frac{\pi \Delta \gamma}{2 \hbar \omega} \left( 1 - \frac{1}{4 \gamma^2} \right) \right) \left( \frac{1}{16 \gamma^2} \right)^k. \quad (4)$$

where $\phi$ denotes Dawson’s integral. In this case electron has time for many oscillations in the binding potential before being ionized.

2.2 Impact ionization

Impact ionization takes place by highly energetic electrons in the conduction band, which can initiate an avalanche process. These free electrons of high kinetic energy may transfer sufficient energy to valence electrons to overcome the ionization potential. Impact ionization leads to a rapid growth in the number of free electrons in the conduction band. Returning to Eq. (2), under the flux-doubling approximation, $\alpha$ is given by [15]

$$\alpha = \frac{2p}{e\phi \int_0^{U_p} 1/\kappa(\varepsilon) d\varepsilon}, \quad (5)$$

where $p$ is constant, $U_p$ is the electron energy threshold for collisional ionization, and $\sigma(\varepsilon)$ is the conductivity per electron

$$\kappa(\varepsilon) = \frac{e}{m} \frac{\tau_m(\varepsilon)}{\left( 1 + \omega \tau_m(\varepsilon) \right)^*}. \quad (6)$$
Here $1/\tau_m$ is the transport (momentum) scattering rate and $\epsilon$ is the electron energy.

3. Experiment

In the present work, we used an IR pump pulse (804 nm, 50 fs) and a weak, time-delayed UV probe pulse (266 nm, 100 fs): fundamental and third harmonic. The UV and IR beams were generated using an amplified Ti:sapphire laser system producing 7 mJ of energy per pulse, at a wavelength of 804 nm, with a repetition rate of 50 Hz and a pulse duration of 50 fs. The third harmonic generation (THG) of the 804 nm beam was obtained by frequency doubling in a BBO crystal and subsequent sum frequency mixing of the residual 804 nm and the created 402 nm in a second BBO crystal, resulting in 266 nm. The pump peak intensity could be varied between 1 TW/cm$^2$ and 50 TW/cm$^2$. The intensity of the probe pulse is clearly below the self-focusing threshold. The linear polarised pump pulse was focused under normal incidence to a spot size of 120 µm ($1/e^2$) inside the medium. A half wave plate (HWP) was used to control the polarization alignment of the IR pump pulse relative to the crystal axes. The UV probe beam was directed through a variable optical-delay line before it was focused to a spot size of ~60 µm ($1/e^2$) using a f = 30 cm fused silica lens. The linear polarised 266 nm pulse was used to probe the refractive index changes induced in the sample by the pump pulse (Fig. 1). The two beams were spatially superposed inside the sample, with a rather small apex angle of about 3 deg. The use of 266 nm pulse enabled the measurement of rather weak changes in the optical constants of the sample on the interaction region. All transmitted 266 nm light was collected on the photodiode.

![Schematic diagram of the optical setup of the crystallographic experiments.](image-url)
4. Results and discussion

![Figure 2](image.png)

Figure 2. Transmission of the probe pulse as a function of the alignment of the IR pump laser polarization to the crystal axis, measured at pump peak intensity \( I = 20 \text{TW/cm}^2 \).

Figure 2 shows the transmission of the UV probe pulse at a fixed delay time \((\Delta t \sim 0 \text{ fs})\) as a function of the rotation angle of the IR-laser electric field vector relative to the LiF crystal axis. It is important to note that the propagation of the probe pulse is not affected by nonlinear effects. As mentioned above the transmission of the probe pulse reflects the pump induced change in the refractive index. The free electrons contribution to the negative change in the refractive index at frequency \( \omega \) can be described by the Drude model \([15]\): \( \Delta n_e \approx -N_e e^2/\varepsilon_0 m_e \omega^2 \); where \( e \) and \( m_e \) are the charge and mass of the electron, \( N_e \) is the electron density, and \( \varepsilon_0 \) is the vacuum dielectric constant. Here it is important to note that the generated free carriers can decay into exciton states \([16]\). However, our data are not affected by exciton formation because the following: (i) in LiF crystal the exciton states are not accessible by the 266 nm photons (high energy levels) \([17–19]\), (ii) their extremely short lifetimes (<3 fs) \([18]\).

As LiF is cubic, one would not expect any significant optical anisotropy. In contrast to that and in agreement with earlier work \([12]\) there is a pronounced dependence on the polarization of the pump pulse. The transmitted probe intensity shows a strong modulation with \( \pi/2 \) rotational periods. The most striking observation is that the modulation amplitude is about 30%. This is more than one order of magnitude larger than that previously observed in \( \alpha \)-quartz (below 1%). So here we observed two noteworthy aspects: (i) \( \pi/2 \) modulation of the transmission, which corresponds to the crystal lattice symmetry; (ii) gigantic amplitude modulation, which can be seen with the naked eye on a screen placed behind the sample.

Let us now discuss the origin of this modulation. Two main effects can explain our observations: (i) light induced transient birefringence, which has been observed in past work \([20]\). In this experiment, the inspection along the optical axis of the crystal was performed under orthoscopic observation conditions between crossed polarizers. It revealed a periodic change of the transmitted intensity when rotating the sample around its axis. (ii) Changes in the multiphoton ionization rate as a function of the alignment angle between the laser electric field and the crystal lattice axis, an effect discussed already by Gertsov et al. \([12]\).

LiF has a cubic unit cell and is optically isotropic and does not show linear birefringence in an ordinary optical field. However, when it is exposed to an intense femtosecond laser field, the nonlinear refractive index shows a transient change. In general, these changes are unequal for two orthogonal crystal axes because they depend on the intensity and the
polarization state of the incident light. This induced phase shift can lead to an angle dependent birefringence at the focus that modulates MPI via the effective intensity.

In general, the light induced phase shifts can be measured through an arrangement where the crystal is placed in between two crossed polarisers. But in the strong nonlinear regime, this parasitic birefringence can lead to a strong MPI modulation, which can be detected in the transmitted light directly behind the crystal [12].

![Graph](https://via.placeholder.com/150)

Fig. 3. Simulation of the pump pulse transmission (chained curve) and the phase shift (dashed curve) as a function of the alignment $\theta$ angle between the laser polarization and the crystal lattice. The transmission angular dependency is caused by an optically induced birefringence of the medium.

In this case, the light induced angle dependent ellipticity will result in a modulation of the transmitted intensity, which is governed by:

$$T = T_0 \sin^2\left(\frac{\Delta \phi}{2}\right) \sin^2(2\theta),$$

$$\Delta \phi = \frac{3\pi L}{3\lambda} n_2 (\cos^2 \theta - \sin^2 \theta).$$

Here $\theta$ denotes the alignment angle between the incident laser polarization and the crystal lattice axis and $\Delta \phi$ is the induced phase shift between the electric field components along the two orthogonal crystal axes. $n_2$ is the nonlinear refractive index, and $L$ and $\lambda$ are the medium length and the incident laser wavelength, respectively.

As can be appreciated from the figure, the transient birefringence induces an oscillation in the transmitted intensity with a rotational period $\pi/4$. This proves that our experimental findings cannot be ascribed to angle-dependent changes in the nonlinear refractive index. Thus, the most plausible explanation of the modulation in the transmitted probe beam is a variation in the ionization rate along different directions in the crystal. This implies that the angular dependence reflects the symmetry of the lattice. The transmitted intensity measured by the photodiode is $T = T_0 + A \cdot (\cos^2 \theta \cdot \sin^2 \theta)$, where $\theta$ is the orientation angle of the IR laser field with respect to the lattice.

These observations agree with results of previous work [12]. The key to understand this dependence is given by resembling the crystal lattice to a dense gas of aligned molecules, where the sensitivity of MPI to the molecule alignment was demonstrated in different previous theoretical and experimental works [16,17]. In gas targets the polarisation dependence is related to the molecular orbital symmetry, whereas in crystals, is related to the band structure. In the case of solids, the ionization can be interpreted according to the Keldysh theory [2,14]. As can be seen from Eq. (3), the dependence of the ionization rate on the orientation of the lattice is governed by the direction-dependent reduced electron mass. Such description of the alignment effect was already proposed and demonstrated in aligned $\alpha$ quartz by Gertsiov et al. [12].
The reduced mass is a concept that is developed specifically for materials with parabolic band-structures. A crude estimate of the reduced mass along the $\Gamma$-X and $\Gamma$-K directions in the crystal can be obtained from the calculated electronic band structure (by) using parabolic fitting. The corresponding directions $\Gamma$-X and $\Gamma$-K in real space are $<100>$ and $<110>$, respectively. The estimated reduced mass along $\Gamma$-X ($<100>$ crystal axis) and $\Gamma$-K ($<110>$ crystal axis) in the reciprocal space are about, $1.07 \, m_e$, $1.67 \, m_e$, respectively. Here where $m_e = 9.11 \times 10^{-31} \, \text{kg}$ is the free electron rest mass. Our data show a maximum absorption when the laser polarisation along $\Gamma$-X and minimum along $\Gamma$-K. In agreement with the theory, where a maximum ionisation along $\Gamma$-X is expected.

As mentioned above the transition between multiphoton ionization and tunnel ionization is characterized in terms of the $\gamma$ Keldysh parameter. In the multiphoton regime $\gamma >> 1$ the ionization is weak and can be described as a perturbative multiphoton process. At very high electric laser fields, in the opposite limit $\gamma << 1$, the potential well formed by the band gap is distorted and photo-induced tunneling may occur. In order to check how much tunneling is connected in the observed modulation we repeated the crystallographic experiments with $400 \, \text{nm}$. In this high frequency regime, the contribution of tunneling decreases with the increase in $\gamma$. As expected the modulation in transmission was not observed at $400 \, \text{nm}$ where four photons are required for ionization. Here it should be noted that in ref [12], the modulation was observed by using lock-In like approach. A principal conclusion can immediately be derived from these data: tunneling ionization plays a significant role in the ionization of the dielectric crystals.

For further analysis, we measured the modulation amplitude at a fixed delay time as a function of the intensity of the pump pulses (Fig. 4). Three regions can be distinguished: For intensities in the range $14 < I < 20 \, \text{TW/cm}^2$, the modulation shows a sharp rise. For peak intensities $20 < I < 35 \, \text{TW/cm}^2$ the amplitude remains almost constant. According to the moving focus model, an increase in peak intensity can lead to the moving of focus toward the entrance of the medium. A crude estimate of the shift of the focus can be made by using the self-focusing length expression [21]:

$$z_f(I) = \frac{0.367 k a_0^2}{[(\sqrt{I/I_{cr}} - 0.852)^2 - 0.0219]^{1/2}},$$

where $k = 2\pi/\lambda$ is the wave number, $a_0$ is the spot size of the pump beam, and $I_{cr}$ is the critical pump Intensity. A peak intensity of $20 \, \text{TW/cm}^2$ gives a shift of $\sim 300 \, \mu\text{m}$. The fact that the magnitude of the modulation does not change with the propagation depth indicates that light
induced birefringence does not contribute to the angle-dependent ionization. This is a further confirmation that the multiphoton ionization rate is dependent on the alignment angle.

![Figure 5](image)

**Fig. 5.** Normalized 266 nm transmitted intensity versus pump-probe delay time; pump peak intensity $I = 20$ TW/cm$^2$. The red solid line is a simulated cross correlation of the IR and 266 nm.

Figure 5 shows the time evolution of the transmitted intensity of the probe pulse. We also include a simulated cross correlation of mid-IR pump and 266-nm probe pulses. Positive time delay corresponds to the IR pump preceding the probe pulse. The data show that the transmission intensity decays on a time scale much larger than the rise time of the cross correlation curve, indicative of the avalanche nature of this process. The free carriers relax within several hundreds femtosecond after the excitation. Our measurements show that the electronic avalanche is the dominant excitation mechanism, the multiphoton absorption only providing the seed electrons for this avalanche, which is in good agreement with previous optical measurements on fused silica [6,10]. In order to check this assumption, we repeated the crystallographic experiments at subsequent delays $t \sim 300$ fs. We found that the modulation in transmission is present. This is a clear indication that multiphoton absorption provides the seed electrons for avalanche ionization.

5. Conclusion

In summary, we report femtosecond crystallography measurements of the ionization rate dependence on the alignment of LiF crystal to the laser polarization. The observed transmission modulation was explained by investigating the direction dependent reduced electron mass. We have emphasized that tunneling plays a significant role in free carrier generation in dielectrics. Furthermore, we have shown that the free-electron gas is formed mainly by avalanche ionization whereas multiphoton/strong-electric-field ionization only provides the seed electrons for this avalanche mechanism.

It should also be possible to apply multiphoton crystallography to orthoscopic techniques, thus enabling a wide variety of new experimental investigations in attosecond science [22].

Acknowledgements

We gratefully acknowledge financial support from the Deutsche Forschungsgemeinschaft (SFB 613) and the discussion with N. Müller.