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Item Type	Article		
Authors	Werner, Kevin; Hastings, Michael G; Schweinsberg, Aaron; Wilmer, Brian L; Austin, Drake; Wolfe, Christopher M; Kolesik, Miroslav; Ensley, Trenton R; Vanderhoef, Laura; Valenzuela, Anthony; Chowdhury, Enam		
Citation	Kevin Werner, Michael G. Hastings, Aaron Schweinsberg, Brian L. Wilmer, Drake Austin, Christopher M. Wolfe, Miroslav Kolesik, Trenton R. Ensley, Laura Vanderhoef, Anthony Valenzuela, and Enam Chowdhury, "Ultrafast mid-infrared high harmonic and supercontinuum generation with n2 characterization in zinc selenide," Opt. Express 27, 2867-2885 (2019)		
DOI	10.1364/0E.27.002867		
Publisher	OPTICAL SOC AMER		
Journal	OPTICS EXPRESS		
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Download date	27/08/2022 18:24:48		
Item License	http://rightsstatements.org/vocab/InC/1.0/		
Version	Final published version		
Link to Item	http://hdl.handle.net/10150/632502		



Ultrafast mid-infrared high harmonic and supercontinuum generation with n_2 characterization in zinc selenide

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Abstract: Polycrystalline ZnSe is an exciting source of broadband supercontinuum and highharmonic generation via random quasi phase matching, exhibiting broad transparency in the mid-infrared $(0.5-20\,\mu m)$. In this work, the effects of wavelength, pulse power, intensity, propagation length, and crystallinity on supercontinuum and high harmonic generation are investigated experimentally using ultrafast mid-infrared pulses. Observed harmonic conversion efficiency scales linearly in propagation length, reaching as high as 36%. For the first time to our knowledge, n_2 is measured for mid-infrared wavelengths in ZnSe: $n_2(\lambda = 3.9\,\mu m) = (1.2\pm 0.3) \times 10^{-14} \, cm^2 / W$. Measured n_2 is applied to simulations modeling high-harmonic generation in polycrystalline ZnSe as an effective medium.

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1. Introduction

Nonlinear optics in polycrystalline zinc selenide (poly-ZnSe) has been studied extensively [1–4], including mid-infrared (MIR) supercontinuum (SC) generation [5] and high harmonic generation (HHG) [6]. Spectral broadening of the harmonics beyond the transform limited bandwidth can result in spectral overlap between the harmonics, or inter-harmonic continuum (IHC), which is attributed to cross phase modulation (XPM) [6].

Isotropic polycrystalline materials such as poly-ZnSe exhibit random quasi-phasematching (RQPM) [7–10]. Any medium with non-zero $\chi^{(2)}$ exhibits 3-wave mixing, where the phase mismatch, $\Delta k = k_3 - k_2 - k_1$ determines the direction of mixing process between the photons in waves 1, 2 and 3. The criterion $\Delta k L_{coh} = \pi$ determines the coherence length L_{coh} of the process, and propagation through a crystal longer than L_{coh} reverses the wave-mixing (e.g. $\hbar\omega_1 + \hbar\omega_2 \rightarrow \hbar\omega_3$ reverses to $\hbar\omega_3 \rightarrow \hbar\omega_1 + \hbar\omega_2$). In a periodically poled crystal, after every L_{coh} , the orientation of the crystal is flipped so that Δk reverses sign, resulting in a high nonlinear field gain, $E_{nl} \propto N$, where N is the number of periods in a periodically poled crystal. However, such periodic poling can be quite expensive and not yet possible for materials like ZnSe. However, even though in poly-ZnSe crystal grains are randomly oriented, a nonlinear gain of $E_{nl} \propto \sqrt{N}$, where N is the number of crystal grains participating in the mixing process [9]. The usual limitations of phase mismatch are thus extended, resulting in generated field bandwidths which are only limited by the transparency window of the material [9]. Thus,

RQPM is a promising isotropic approach for broadband three wave mixing applications with a wide spectral range [9] achieved at significantly lower cost compared to nonlinear frequency conversion processes from expensive single crystals cut in specific orientation with tight angular tolerance or even more expensive periodically poled crystals of very limited choice. This is especially true in mid to long wave IR regime, with the availability of poly-ZnSe.

Longer wavelengths lead to increased spectral broadening through self-phase modulation (SPM) and filamentation in poly-ZnSe [11–13]. As a result, interest in the MIR nonlinear properties of RQPM and poly-ZnSe has continued to grow [14–17]. Linear scaling of harmonic efficiency with crystal length has been demonstrated experimentally to lead to high conversion to the harmonics (19% second harmonic, 0.5% third harmonic) [12].

MIR ultrafast nonlinear optics contains a diverse array of applications in ultrafast spectroscopy [17–19]. As Cr and Fe doped ZnSe are proving to be exciting laser materials for broadband amplification in MIR, non-linear response to MIR pulses on ZnSe is also relevant from that perspective [20]. Recent progress has also been made in the field of efficient, broadband harmonic generation [21]. MIR RQPM is another way to generate SC/HHG with high efficiency and large spectral bandwidths.

In this work, we observed SC generation and HHG/IHC to 7th order via RQPM using ultrafast MIR pulses in poly-ZnSe, extending previous results [12,17] to longer wavelengths. Contrasting with previous works [6,11,13,14], in this study both the transmitted fundamental and generated harmonics were studied experimentally and theoretically. Sample thickness was varied, with a maximum thickness of 4 cm. This has allowed us to investigate experimentally the interplay between changes in the fundamental and HHG/IHC. By varying the input pulse power, intensity, wavelength, and propagation distance, we explored the conditions under which SC, HHG/IHC, and filamentation occur. In our experiments, we clearly demonstrate these processes occur within a non-perturbative regime of harmonic generation. We explore MIR nonlinear propagation effects with up to 4 cm propagation lengths for the first time. Harmonic efficiency was found to follow a linear scaling with increasing propagation length, leading to harmonic efficiency as high as 36% (2nd through 7th). To the best of our knowledge, this is the highest harmonic efficiency reported in ZnSe. Our experiments were repeated with single crystal ZnSe (single-ZnSe), where harmonics only up to order three were generated, exhibiting a smaller spectral bandwidth for individual harmonics and greater than an order of magnitude smaller harmonic efficiency in a clearly demonstrated perturbative regime. Even though $n_2(MIR)$ may be very different for nearinfrared (NIR) wavelengths, the approximation $n_2(NIR) \approx n_2(MIR)$ is still used in the field

as an estimate due to lack of experimental data at MIR wavelengths. In this work, we have measured experimentally for the first time $n_2 (\lambda = 3.9 \,\mu m) = (1.2 \pm 0.3) \times 10^{-14} \, cm^2 / W$ with

good matching to theoretical predictions. Our experimental result for n_2 is used in gUPPE simulations of nonlinear light propagation, where we qualitatively reproduce all the results seen in poly-ZnSe.

The goal of our simulation work is to shed light on the process of the strong, nonperturbative scaling HHG and SC generation in poly-ZnSe as well as to test whether an effectively scalar medium model can capture the main physics. The model can predict the experimentally observed trends in harmonic generation as a function of input power and propagation distance, which it mainly attributes to cascaded second and third order nonlinearities [22], free carrier generation and random quasi-phase matching.

2. Experimental setup

A continuously tunable, multistage ultrafast Extreme MIR (EMIR) optical parametric amplifier (OPA) ($\lambda = 2.5 - 4.5 \,\mu m$, $\tau_{pulse} \sim 200 \, fs$, max energy $35 \,\mu J / pulse$) pumped at a 500

Hz repetition rate by a Ti:Sapphire regeneratively amplified laser (OSU Gray Laser [23,24], 3 mJ/pulse, 30 – 300 fs, center wavelength of 773 nm) was designed and built for the generation of MIR pulses. The OPA uses white light seed generated from focusing a beam of several μ J/pulse pickoff from the 773 nm driver laser pulses onto a 3 mm sapphire crystal. The pJ seed pulses are then amplified in three stages via parametric amplification in non-linear crystals: Stage 1, and 2 with two separate 1 mm thick KNbO₃ crystals, and Stage 3 with a 2 mm thick KTiOAsO₄ (KTA) crystal. The beam profile of the OPA is characterized using a MIR camera (Dataray, Wincam-D-FIR2-16-HR). The pulse duration across wavelength is characterized by an AgGaS₂ (AGS) crystal based second harmonic autocorrelator and by frequency-resolved optical gating (FROG). The MIR pulses were then focused into the sample, with the resulting harmonics and transmitted fundamental collected and analyzed. An experimental schematic can be seen in Fig. 1(a). The central wavelength of the MIR pulses was chosen to be either $\lambda_0 = 3.4 \,\mu m$ or $\lambda_0 = 3.8 \,\mu m$.



Fig. 1. Experimental Schematics. (a) Harmonic generation setup with MIR pulses from EMIR OPA. MIR pulse energy is controlled using a waveplate (WP) polarizer (P) combination. MIR light is focused by lens L1 onto a ZnSe sample. A collection optic (L2) was used to collimate the transmitted light before filtering (F) is applied within the filter plane. The light is then focused via a coupling lens (L3) onto the detector. For harmonic efficiency measurements, pulse energy was measured at points E_1 and E_2 . (b) Setup of non-linear index, n_2 measurement with MIR femtosecond pulses using z-scan technique.

A waveplate/polarizer combination is used to vary the MIR pulse energy ($E_1 = 1-10 \,\mu J$, $P_{pulse} \approx 5-50 \,MW$). The MIR pulses are focused to a spot size of 98.5 μm full width at half maximum (FWHM) as measured in air (Rayleigh range $z_R \sim 5mm$) using a (CaF₂, $f(MIR) = 105 \,mm$) lens (L1 in Fig. 1(a)). Peak intensity was varied from $I_0 \approx 45-460 \,GW/cm^2$, far below the MIR laser induced damage threshold of ZnSe. The critical power for self-focusing, P_{cr} , is an often-used metric to define different regimes of SC generation and filamentation [12,17]. Here, the MIR pulse power is varied from $(P/P_{cr})(\lambda = 3.4 \,\mu m) \approx 4.2-42$ and $(P/P_{cr})(\lambda = 3.8 \,\mu m) \approx 3.4-34$.

To probe the effect of higher peak intensities while keeping the pulse power fixed, L1 was replaced with a 20 mm focal length lens, leading to a FWHM spot size of $\sim 24 \,\mu m$. Here, intensities of $I_0 \approx 0.77 - 8 \, TW \,/\, cm^2$ are accessible and $\lambda_0 = 3.3 \,\mu m$ was used.

Samples used were various thickness (1 mm, 5 mm, 10 mm, 20 mm, 40 mm) poly-ZnSe samples (grain size range between 20 and 100 μ m, Stingray Optics) or a 1 mm thick single-ZnSe sample (MTI Crystals). The single-ZnSe sample orientation was adjusted to maximize the generated 2nd harmonic intensity. In the case of 20 mm focal length L1, the 5 mm thick poly-ZnSe sample was placed with its center 20 mm from L1.

Transmitted MIR pulses were collected and collimated in a second CaF₂ 100 mm focal length lens (L2 in Fig. 1(a)). In the filter plane, filtering was applied, and any relevant filter transmission was applied to the data in post processing. MIR pulses were then coupled into a calibrated MIR spectrometer (Acton Research with FLIR cooled focal plane array) via a third lens (L3 in Fig. 1(a)), which was found to be opaque to the harmonics. The observable spectral range for the spectrometer was $\lambda = 3-5 \mu m$, with a variable spectral observation window.

In another configuration, L2 is replaced with a 10X Mitutoyo Plan Apo NIR Infinity Corrected Objective, found to be opaque to MIR pulses. This objective is used to collect the harmonics, and its response curve was included for the spectral calibration of harmonics in post processing. In this case, no filtering is applied, instead the light is collected by L3 and coupled into a fiber before being sent to either a visible (VIS) or NIR spectrometer (together spanning the spectral range $\lambda = 0.5 - 1.7 \,\mu m$), replacing "Detector" in Fig. 1. The fiber position relative to the harmonic pulses is kept fixed while switching spectrometers. The VIS and NIR spectrometers are cross-calibrated using the overlap between their spectral windows combined with relative irradiance calibrations.

In a similar setup for near field intensity distribution measurements of the harmonics, the detector in Fig. 1 is replaced with a NIR camera, and neutral density filtering (F) is applied. The filter transmission is considered in post processing. L1 and L2 are configured such that the back surface of the sample is imaged onto the camera.

For determining the efficiency of harmonic generation, the MIR input pulse energy is measured at position E_1 in Fig. 1(a). The harmonic energy is measured at position E_2 , since the objective L2 is not transmissive to MIR wavelength to any level detectable by our energy meter, even without a sample present. The known transmission curves for each optic (L2, L3) are accounted for when calculating harmonic energy.

For the n_2 characterization of ZnSe, we used the conventional Z-scan technique [25] at the U.S. Army Research Laboratory's Adelphi Laboratory Center (ALC). The schematic of the experimental setup is shown in Fig. 1(b). A Ti:sapphire laser system (Coherent, Hidra-F-100) pumped an OPA (Light Conversion, TOPAS-Prime-HE), which was then used for DFG (2 mm thick Type II KTA) to obtain $\lambda = 3.9 \,\mu m$ pulses. The DFG pulses were spatially filtered by focusing into a 180 μm diameter single-diamond pinhole using an all-reflective geometry. A ZnSe wedge was used as a pickoff for the reference detector. The pulses were subsequently focused into the sample via a 150 mm ZnSe focusing lens.

To determine the energy used in the Z-scan runs, the reading from a spectrally flat broadband THz radiometer with linearity ranging from 0.1 μ W to 20 mW was calibrated with a pyroelectric detector (Ophir, PE10) near the output of the DFG where the energy is relatively high (~0.5 mJ). The radiometer was then placed directly in front of the sample (after the spatial filter and pickoff wedge) without the presence of any filters and a reading was taken to obtain the actual energy. Attenuation was achieved by using calibrated Ge neutral density (ND) filters having a spectrally flat response from 2 to 18 μ m. The minimum beam waist was measured to be 48 μ m gaussian waist radius by one-dimensional knife-edge scans. The pulse width was measured by second-order intensity autocorrelation in a 400 μ m thick Type I AgGaS₂ crystal and determined to be 260 fs (FWHM).

3. Numerical modeling of optical filamentation

We use the gUPPEcore simulator implementing the unidirectional pulse propagation equations (UPPE) [26]. In a scalar and/or semi-vectoral approximation motivated above, the optical field evolution satisfies UPPE, which incorporates nonlinear response of the medium in polarization and current density.

The nonlinear polarization includes both the second-order and third-order nonlinearity. The latter is implemented as usual and parameterized by the nonlinear index for which we use

the experimental value. The second-order nonlinearity is described as if in an effective isotropic medium like so (note that E(t) represents the full electric field encompassing all harmonic orders and supercontinuum);

$$P_2(t) = r(z)\varepsilon_0 d_{\rm eff} E(t)^2 \tag{1}$$

where d_{eff} stands for the effective nonlinear coefficient, and the random function r(z) represents passage through different grains of the polycrystalline medium. In this work we switch it on or off randomly with a correlation length chosen to mimic the grain size. Note that we use the same r(z) for all cross-section points which is one of the simplifications to be relaxed in a more sophisticated model. The simulations were performed for several different parameter choices. Here we show results for $d_{eff} = 15$ pm/V and the grain-size related correlation length of $70 \,\mu$ m. For comparison, the poly-ZnSe used in experiment with 20-100 μ m grain size has estimated coherence lengths, $L_{coh} \sim 51$, 17, and 9.6 μ m for 2nd, 3rd and 4th harmonic generation via $\chi^{(2)}$ processes, respectively.

The motivation for a simplified model stems from the computational complexity involved in proper space- and time-resolved simulations of a poly-crystalline medium with both second and third-order nonlinearities. The canonical choice would be to resolve a realization of random packing of single-crystal grains, simulating vectoral pulse propagation in each. Multiple runs would be required to account for (or average over) random orientations and sizes of the grains, and a very fine spatial-grid resolution would be needed to ensure proper convergence.



Fig. 2. Experimental measurements of transmitted fundamental spectral intensity (a) mapped as a function of MIR pulse (center wavelength $\lambda = 3.8 \,\mu m$) energy focused onto a 5 mm thick poly-ZnSe. Linear interpolation is used for ease of reading. The dotted black line at the top boundary represents a lineout presented in (b) (black curve), for an input MIR pulse energy ($E_1 = 10.6 \pm 0.1 \,\mu J$,). (b) Comparing MIR spectral broadening in 5 mm poly-ZnSe and single crystal ZnSe data (red dotted line $E_1 = 10.4 \,\mu J$), along with that of the laser without any sample (green dotted line).

As previously discussed, a most important ingredient in HHG and SC generation in poly-ZnSe is expressed in the idea of RQPM. What we put forward here is marrying this concept with the space- and time-resolved simulations involving an effective scalar model for the second-order nonlinear polarization. Other components of the model, including carrier generation, carrier-induced defocusing, third-order nonlinearity, chromatic dispersion, and wavelength-dependent linear optical loss have been accounted for utilizing only parameters taken from measurements. As such, the description of the effective second-order nonlinearity remains the only adjustable parameter.

To further probe the underlying physics, we restrict our simulations with axial symmetry. In such a geometry, only a single filament is possible, unlike in our experiments where multiple filamentation can occur for the longest propagation distance. However, while we lose here any one-to-one mapping between experimental and simulated pulse energies, we trust that the underlying physics remains the same.

4. Results and discussion

Modulations to the fundamental were observed, with SC generation occurring at higher intensities or with thicker samples. Harmonics were generated out to 7th order. The input MIR pulse power, central wavelength, and intensity were varied, resulting in modifications to both the SC and harmonic spectrum, such as spectral broadening or blue shifting. Power scaling effects were investigated. Single-ZnSe vs poly-ZnSe are compared directly to highlight the unique nature of RQPM. Next, the effect of propagation length was investigated. Measurements of the near field intensity profiles of the 2nd harmonic, third harmonic, and IHC were performed, showing evidence of filamentation in the sample.



Fig. 3. Experimental spectral measurements of transmitted generated harmonics intensity as a function of MIR pulse energy in a 5 mm thick poly-ZnSe sample. (a) Spectral mapping for harmonics resulting from $\lambda = 3.8 \,\mu m$ MIR driver laser. Linear interpolation is used for ease of reading. The dotted black line in (a) represents a lineout presented in (b) (black curve), for an input MIR pulse energy ($E_1 = 10.6 \pm 0.1 \,\mu J$).



Fig. 4. (a) Spectral intensity of harmonics generated from a MIR driver at $\lambda = 3.3 \,\mu m$ focused onto a 5 mm thick poly-ZnSe sample (black line, $E_1 = 8.17 \,\mu J$) and a 1 mm thick single crystal ZnSe sample (red dotted line, $E_1 = 8.04 \,\mu J$). (b) Spectral broadening in 5 mm poly-ZnSe with $\lambda = 3.4 \,\mu m$ driver with $E_1 = 7.02 \,\mu J$ for the fundamental broadening at lower intensity (black line) and higher intensity (blue dash-dotted line, $E_1 = 7.35 \,\mu J$), with 98.5 and 24 μ m FWHM focal spots, respectively. Green dotted lines represent the laser spectrum with no sample.

4.1 Effects of MIR pump parameters

In Fig. 2, Fig. 3, and Fig. 4 experimental spectra of both transmitted MIR fundamental and generated harmonics from a 5 mm thick poly-ZnSe and a 1 mm thick single-ZnSe sample are presented. The effects of varying the input MIR power for a MIR driver with central wavelength of $\lambda = 3.8 \,\mu m$ are shown in Fig. 2. Lineouts of fixed pump power for two different MIR pump wavelengths, $\lambda = 3.4, 3.8 \,\mu m$, are shown. With these central wavelengths, regimes of 8- and 9- photon absorption are probed. In Fig. 2(a), the $\lambda = 3.4 \,\mu m$ lineout also overlays the effect of increasing the MIR input pulse peak intensity while keeping pump pulse power fixed. For the lineouts, the input pulse power was chosen such that $P_{pulse} \approx 34P_{cr}$ by selecting $E_1(\lambda = 3.4 \,\mu m) = 7.6 \pm 0.6 \,\mu J$ or $E_1(\lambda = 3.8 \,\mu m) = 10.5 \pm 0.2 \,\mu J$. In estimating P_{cr} , the nonlinear index of refraction n_2 was estimated [12], resulting in

$P_{cr}(\lambda = 3.4, 3.8 \,\mu m) = 1.18, 1.47 \, MW$, respectively.

Figure 3(a) clearly shows two distinct pump power regimes in spectral broadening of the harmonics, despite a relative lack of broadening dynamics in the fundamental. Potential reasons for the lack of broadening dynamics in the fundamental include: energy losses from linear absorption, free carrier absorption [27], depletion from harmonics generation, or inaccuracy of P_{cr} due to lack of MIR data [12]. For $E_1 \lesssim 5 \mu J$ no spectral broadening is observed in the harmonics. While for $E_1 \gtrsim 5 \,\mu J$ broadening occurs like the single filamentation regime in [12]. As an example, the critical power for self-focusing of the third harmonic $P_{cr}(\lambda = 1.26 \,\mu m) = 0.16 \,MW$, much lower than that of the fundamental. With total harmonic conversion efficiencies reaching up to 36% (see section 3.3), it is reasonable that this power threshold is exceeded by (for example) the 3rd harmonic. It is possible, supported by the evidence presented in Fig. 2, Fig. 3, and Fig. 4 and by near field intensity profiles (discussed in section 3.4), that filamentation and resulting IHC generation can occur in the harmonics, without SC generation also occurring in the fundamental. IHC is therefore not necessarily caused by XPM, as has been suggested [6]. Application of these results include generation of broadband VIS/NIR light while retaining the spectral profile of the MIR fundamental pump for use in pump-probe or broadband spectroscopy experiments.

The spectra of Fig. 2(b) and Fig. 4(b) compare the $\lambda = 3.8 \,\mu m$ and $\lambda = 3.4 \,\mu m$ cases in the intensity regime of $I_0 \approx 400 \, GW / cm^2$. In terms of spectral modulations about the fundamental, an increased broadening can be seen on the Stokes side for the $\lambda = 3.4 \,\mu m$ case. The $\lambda = 3.4 \,\mu m$ case also exhibits a redshift of the fundamental peak position by around 5 nm. Meanwhile, a clear enhancement of the anti-Stokes side broadening can be seen in the $\lambda = 3.8 \,\mu m$ case (Fig. 2(b)). For both wavelengths, even and odd order broadband harmonic emission, accompanied by IHC, was observed. In the $\lambda = 3.8 \,\mu m$ case, harmonic orders 2-7 were observed, while in the $\lambda = 3.4 \,\mu m$ case harmonics beyond order 6 were not observed, most likely due to the ZnSe transparency cutoff. The $\lambda = 3.8 \,\mu m$ case exhibits a large enhancement of the IHC/broadening of the harmonics, far outweighing the enhancement to the broadening of the fundamental.

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Thickness (mm)	Crystal Structure	Fundamental Spectral Broadening ^b (nm)		Third Harm Broaden	onic Spectral ing ^c (nm)
		$\lambda_0 = 3.8 \mu m$	$\lambda_0 = 3.4 \mu m$	$\lambda_0 = 3.8 \mu m$	$\lambda_0 = 3.4 \mu m$
5	Poly	14	-36 (335 ^d)	52	1
40	Poly	-9	N/A	-47	N/A
1	Single	3	N/A	N/A	-3

Table 1. Spectral Broadening: Absolute Change in Spectral Bandwidth^a

^aFocal spot FWHM ~98.5 µm was used unless otherwise indicated. ^bDefined as change in FWHM bandwidth of fundamental frequency after inserting the sample, with positive changes representing broadening. ^cDefined as difference between measured FWHM bandwidth of third harmonic and expected bandwidth:





Fig. 5. (a) Power scaling analysis. Each row is labeled with the harmonic order, N. Each column is labeled with sample type and thickness. The plots show experimental data (dots) and lines which follow the scaling law $I_N \propto I_0^N$ where I_N is the intensity of the Nth harmonic and I_0 is the intensity of the input MIR fundamental. (b) Generated harmonic intensity for harmonics of various orders: N = 2 (red solid triangle), N = 3 (green solid square), N = 4 (blue empty circle), N = 5 (purple empty triangle), N = 6 (black solid circle). The best linear fit ($I_N \propto I_0^1$) for each harmonic order is shown (solid lines) with colors corresponding to harmonic order matching that of the shapes. The sample used was poly-ZnSe 1 mm thickness.

In perturbative harmonic generation with perfect phase matching, the ideal FWHM bandwidth of generated harmonics $(\Delta\lambda(n) \text{ where n is the harmonic order})$ is related to the FWHM of the fundamental $(\Delta\lambda(0))$ by $\Delta\lambda(n) = \Delta\lambda(0)/(n\sqrt{n})$ [28]. Table 1 outlines the FWHM spectral broadening of the spectra shown in Fig. 2, Fig. 3, and Fig. 4. For the fundamental, spectral broadening is defined as the positive change in FWHM spectral broadening is defined as the positive change in FWHM spectral broadening is defined as the positive change in FWHM spectral broadening is defined as the positive change in FWHM spectral broadening is defined.

as the difference (positive change) between observed and ideal bandwidth. The ideal bandwidth is calculated using the spectral bandwidth of the modulated fundamental. We see that for the $\lambda = 3.4 \,\mu m$ case the 5 mm poly-ZnSe sample yields a third harmonic with a FWHM spectral bandwidth within 1 nm of the ideal case. In stark contrast, in the $\lambda = 3.8 \,\mu m$ case, the 5 mm poly-ZnSe yields a third harmonic with a FWHM spectral bandwidth which is 52nm larger than the ideal case. This shows that under these conditions, a large portion of the harmonic spectral bandwidth is not due to cross phase modulation. This ultra-broadband harmonic generation is an indication of RQPM due to relaxed phase matching conditions in polycrystalline materials [9,10,12].

Despite the lack of blue-shift in the fundamental (and at times even a slight redshift), significant blue shifting occurs in the harmonics, as can be seen by Fig. 2(a). For the $\lambda = 3.8 \,\mu m$ case in scaling the pump pulse energy from $E_1 = 1.6 \,\mu J$ to $E_1 = 12.6 \,\mu J$, a 48 nm blue-shift is observed in the 3rd harmonic. Similarly, in the $\lambda = 3.4 \,\mu m$ case, driving the pulse energy from $E_1 = 2.1 \,\mu J$ to $E_1 = 14.1 \,\mu J$ resulted in a 33 nm blue-shift in the third harmonic.

In Fig. 4(b), the effect of increasing input pump intensity while keeping the pulse power fixed can be seen. Here, the 100 mm focal length lens (L1 from Fig. 1) is replaced with a 20 mm focal length lens. The intensities shown with the 100 mm case varied from $I_{peak} = 250 - 350 GW / cm^2$, while with the 20 mm case the intensity reaches $I_{peak} = 4TW / cm^2$. Here, we note that although the pulse power is still roughly the same relative to P_{cr} , the FWHM spectral bandwidth of the transmitted fundamental increases to 486 nm, generating a SC spectrum spanning from 2.9 to 4.2 μm (Fig. 2d.).

In Fig. 4(a), the transmitted fundamental and generated harmonics in a 1 mm single crystal ZnSe sample are shown. Modulations to the fundamental result in spectral broadening, although to a lesser extent than for the poly-ZnSe case, as can be seen from Table 1 for $\lambda = 3.8 \,\mu m$. Only 2nd and 3rd harmonics were generated when using the single crystal ZnSe sample, and no IHC was observed. Furthermore, the FWHM spectral bandwidth of the harmonics generated by single crystal ZnSe is smaller than the poly-ZnSe case (Table 1) and falls short of the ideal theoretical case. This is because the ideal case assumes perfect phase matching (Fig. 4(a). Using a 5 mm thick single crystal ZnSe sample, since generated harmonics in a thicker single crystal ZnSe sample would undergo further pulse splitting due to group velocity mismatch [29]. In our case, the choice of 1 mm was based primarily on availability. In contrast, poly-ZnSe samples are widely available, cost effective, and do not require considerations relating to phase-mismatch.

Power scaling analysis was performed on both single-ZnSe and poly-ZnSe for the case of $\lambda = 3.3 \,\mu m$. The results are displayed in Fig. 5. The input MIR pump pulse energy was varied from $E_1 \approx 2-12 \,\mu J$. In the 1 mm thick single crystal case (Fig. 5(a)), the power scaling is perturbative for both SHG and THG. SHG and THG for 1 mm thick poly-ZnSe deviates from the respective scaling laws once the pulse energy exceeds $E_1 \approx 10 \,\mu J$ (Fig. 5(a)). Higher order harmonics generated in poly-ZnSe (4th, 5th, and 6th order) all deviate from the respective power laws. For comparison, the experiments were performed with 1 cm thick poly-ZnSe (Fig. 5(a)). With the longer propagation distance, even the SHG and THG was found to vary from the respective power law for all input MIR pulse energies. Figure 5(b) shows that for higher input energies harmonic orders begin to scale the same way, in this case exhibiting a linear increase with the pulse energy. This type of behavior is typically attributed to non-perturbative physics in bulk crystals [30].

While harmonics beyond the band edge were not detected as in the case of ZnO [30], we are clearly accessing a non-perturbative regime of harmonic generation, either by increasing the pulse energy, propagation distance, or both. However, unlike with ZnO, we do not see harmonics beyond the band edge, likely due to the sharp cutoff in linear transmission of ZnSe in the visible. However, as has been pointed out before [14], scattered blue light can be seen by eye in reflection which could indicate the presence of higher order harmonics which are greatly attenuated in forward propagation.

4.2 Propagation effects: varying sample thickness

The sample thickness was varied (1 mm, 5 mm, 10 mm, 20 mm, 40 mm) with an input MIR pulse energy ($\approx 8.8-9.2 \,\mu J$) and wavelength ($\lambda = 3.8 \,\mu m$) to investigate the effect of propagation length (Fig. 6). Modulations in the fundamental show a significant increase in broadening for the 10 mm case, which continues to broaden up to the 40 mm case (Fig. 4(a)). A redshift in the central frequency of up to 55 nm (40 mm thickness) is also observed.

Figure 6(b) shows spectral broadening of the fundamental relative to the free space spectrum (no sample present). The sharp cutoff at $\lambda = 4.2 \,\mu m$ is believed to be due to atmospheric CO₂ absorption. A similar amount of broadening can be achieved, as that seen in Fig. 4(b) for the high intensity case, by increasing the propagation length to 40 mm while keeping the input intensity constant. Harmonics generated in 4 cm thick poly-ZnSe are shown in Fig. 6(c). In this case the spectral broadening of the third harmonic is far less than that of the 5 mm sample case (Table 1). While new spectral content is generated in the fundamental, analysis of FWHM spectral bandwidth indicates narrowing. Note that the second harmonic is mostly cut off in the figure; it falls outside the spectral region observable by our spectrometers.



Fig. 6. Varying the propagation length with different thickness poly-ZnSe samples (1,5,10,20,40 mm). A $\lambda_{MIR} = 3.8 \,\mu m$ fundamental with a fixed pulse power results in SC generation and harmonics generation within the sample. (a) Color map of spectral modulations to the MIR fundamental due to propagation through poly-ZnSe samples of various thicknesses. Linear interpolation is used for ease of reading. (b) Comparison of the MIR fundamental spectrum after propagating through 40 mm poly-ZnSe (solid black line) to the unperturbed MIR fundamental spectrum (green dotted line). (c) Harmonics generated from a 40 mm poly-ZnSe sample.

The harmonic efficiency as a function of propagation distance through poly-ZnSe for a fixed pump wavelength ($\lambda = 3.3 \,\mu m$) is shown in Fig. 7. As expected for RQPM materials,

the efficiency scales linearly with the propagation distance. Here, we confirm this out to 40 mm propagation distance for the first time. Linear scaling is found for several different MIR pump pulse energies (Fig. 7(a).). For each pulse energy, we found that the shortest propagation lengths were outliers to the linear scaling.

A harmonic efficiency as high as 36% was recorded using the 40 mm poly-ZnSe sample (Fig. 7(a).). We define harmonic efficiency as the ratio of total harmonic pulse energy to input pulse energy. Large efficiency is expected for RQPM processes due to the relaxation of phase-mismatch conditions. The linear scaling of efficiency with propagation distance makes these materials promising for ultra-efficient harmonics generation in materials. The high efficiency is exhibited in Fig. 7(b). In the image, invisible MIR pulses generate NIR and visible harmonics with 36% efficiency in a 40mm poly-ZnSe sample.



Fig. 7. Harmonic efficiency in poly-ZnSe with a fixed fundamental wavelength $\lambda = 3.3 \,\mu m$. (a) Harmonic efficiency as a function of propagation distance (sample thickness) for three different input pump energies: $14.4 \,\mu J$ (black squares), $10.1 \,\mu J$ (green triangles) $6.1 \,\mu J$ (red circles). (b) Camera image of ultra-efficient harmonic generation in a 40 mm thick poly-ZnSe sample.

In comparison, we note that under identical pump conditions, the harmonic efficiency in single crystal ZnSe was not measurable using our energy meter, which has a pulse energy threshold of around $E_{threshold} = 0.3 \mu J$. Since the harmonic pulse energy was not detectable even with the highest MIR pump pulse energy of $12 \mu J$, we can say that the harmonic conversion efficiency for single crystal ZnSe is $\leq 2.5\%$. In other words, the efficiency is more than an order of magnitude lower than the poly-ZnSe case.

4.3 Near field intensity profiles: filamentation

Near field intensity profiles were recorded by imaging the back surface of poly-ZnSe samples using the generated harmonics and IHC as the illumination source (Fig. 8). The input pulse energy was kept fixed at $E_1 \approx 9 \,\mu J$. The fundamental wavelength was also kept fixed $\lambda = 3.3 \,\mu m$. Notch filters were used to isolate the SHG, THG, and IHC intensity profiles.

Dot patterns reminiscent of RQPM [8] can be seen in both the THG (Fig. 8(a)-(b)) and SHG (Fig. 6(d)-(e)). In neither the 10 nor 20 mm thickness case does the near field intensity profile indicate the presence of filamentation.

Considering the 40 mm thickness case, both THG (Fig. 8(c)) and SHG (Fig. 8(f)) exhibit multiple filaments of $50 \mu m$ FWHM in size. Multiple filamentation is typically correlated with a large increase in spectral broadening, as was observed for the 40 mm case (Fig. 6(b)).

In section 3.1, we discussed the presence of IHC without the corresponding SC generation that would be expected if XPM were the mechanism of IHC generation (Fig. 2(b)). By inspecting Fig. 8(i), we can see that IHC spatial profile is entirely matched with those of the filaments in the 40mm case, indicating that the IHC may be generated by the filaments. With the two shorter propagation distances (Fig. 8(g)-(h)), it appears a single filament is formed, of approximate size $100 \,\mu m$ FWHM at the back face of the sample. Again, the IHC matches the

intensity profile of the filament quite well, indicating the filament may be the primary source of IHC.



Fig. 8. Near field intensity profiles imaged at the output face of the sample. Input MIR pulse parameters were fixed at $E_1 \approx 9 \,\mu J$ and $\lambda_0 = 3.3 \,\mu m$. Notch filters are used to isolate THG, SHG, and IHC. THG is isolated with the use of a bandpass filter centered at $\lambda = 1100 \pm 5 \,nm$ (a)-(c). SHG is isolated using bandpass filter centered at $\lambda = 1650 \pm 6 \,nm$ (d)-(f). IHC is isolated using a bandpass filter centered at $\lambda = 1250 \pm 5 \,nm$ (g)-(i). Each column represents a different propagation length (sample thickness): 10 mm (a), (d), (g); 20 mm (b), (e), (h); and 40 mm (c),(f),(i). Each image is presented with a universal transverse spatial scale and a universal logarithmic intensity scale for comparison.

Power scans were performed for a single sample thickness (40 mm) and fixed wavelength $\lambda = 3.3 \,\mu m$ (Fig. 9). In Fig. 9(e), only one filament was observed. This indicates that the transition from single to multiple filamentation in the 40 mm thick poly-ZnSe sample is between 2.45 and 3.07 μJ under these conditions.



Fig. 9. Near field intensity profiles of a 40 mm thick poly-ZnSe samples with $\lambda = 3.3 \,\mu m$. Each image was taken with a different input MIR pump pulse energy: (a) 9.4, (b) 8.9, (c) 6.0, (d) 3.1, (e) 2.5 μJ .

4.4 Z-scan measurements

The linear transmission of a 2 mm thick ZnSe window (ISP Optics, ZC-W-25-2) was measured by a Perkin Elmer Lambda 950 UV-Vis spectrometer and a Nicolet 8700 FTIR spectrometer, respectively. Using the real part of the refractive index (n) of 2.43 [31], the linear transmission indicates minimal absorption at $\lambda_0 = 3.9 \,\mu m$ and, thus, the imaginary component of the refractive index, κ , can be assumed to be $\ll 10^{-5}$.

The results of Z-scan measurements are shown in Fig. 10. Z-scans were performed on the same 2 mm thick window at three different energies (Fig. 10(a)). Z-scan fits of $(0.9\pm0.4)\times10^{-14} cm^2/W$, $(1.5\pm0.38)\times10^{-14} cm^2/W$, and $(1.25\pm0.31)\times10^{-14} cm^2/W$ were obtained for an input energy of 57 nJ $(4.7 GW/cm^2)$, 115 nJ $(9.5 GW/cm^2)$, and 230 nJ (19 GW/cm^2), respectively. Thereby, an average n_2 of $(1.2\pm0.3)\times10^{-14} cm^2/W$ was measured for ZnSe at 3.9 μ m. This value agrees within error of the theoretical prediction given in reference [32] using a bandgap energy of 2.71 eV, the dispersion relation given in reference [31], and the parameters, K = 3100, K' = 1.5×10^{-8} , and $E_p = 21.4 eV$, which are explicitly defined in reference [32]. Figure 10(b). shows our MIR measurement for n₂ alongside the theoretical curve. Various measurements of sinle-ZnSe and poly-ZnSe in the NIR regime are also shown.

While the theoretical prediction shown in Fig. 8b shows a relatively flat n_2 dispersion from ~2 to 5 μ m, this was not to be expected for shorter wavelengths. As alluded to earlier, the lack of experiments in the MIR led researchers to assume $n_{2,\text{NIR}} = n_{2,\text{MIR}}$. To our knowledge, this is the first experimental measurement of ZnSe in the MIR, thus confirming the flat nonlinear dispersion predicted by theory at least out to 3.9 μ m.

If we take $n_2 = 1.2 \times 10^{-14} \ cm^2 / W$ from our experimental results as a better approximation of n_2 , this results in a smaller P_{cr} than previously considered. Under the approximation $n_{2,MIR} \approx n_{2,NIR}$ we found $P_{cr} (\lambda = 3.4, 3.8 \ \mu m) = 1.18, 1.47 \ MW$. Considering $n_{2,MIR} \approx n_2 (\lambda = 3.9 \ \mu m)$, we find $P_{cr} (\lambda = 3.4, 3.8 \ \mu m) = 0.59, 0.74 \ MW$. This approximation

indicates that our experiments (which ranged from $P_{pulse} \approx 5-50 MW$) are well above the critical power for self-focusing. The authors in reference [12] found a filamentation threshold of 3 MW for $\lambda = 2.4 \ \mu m$. However, using the $n_{2, MIR} = n_{2, NIR}$ approximation, i.e. the n_2 value from [33] they calculated a critical power of 0.59 MW, well below their measured filamentation threshold. The authors suggest that one reason for this discrepancy may be lack of knowledge of $n_{2,MIR}$. However, if we apply our experimental value for $n_{2,MIR}$ under the approximation $n_2 (\lambda = 3.9 \ \mu m) = n_2 (\lambda = 2.4 \ \mu m)$ we find $P_{cr} (\lambda = 2.4 \ \mu m) = 0.29 MW < 0.59 MW$, which is not closer to the author's measured value of 3 MW. The theoretical curve suggests that this approximation is valid (Fig. 10(b)).



Fig. 10. (a) Z-scan measurements for $\lambda_{MIR} = 3.9 \,\mu m$ and a 2 mm thick poly-ZnSe Window. Each color/shape represents a different input MIR pump energy and fit, offset for clarity, as indicated in the legend. The solid lines of corresponding color represent the fit used to extract n_2 . (b) Theoretical curve for n_2 [32] (solid line), measured n_2 of single crystal ZnSe at 1200 nm and 1950 nm (solid green circles [34]), single crystal ZnSe at 1310 and 1550 nm (solid upside down red triangles [35]), measured n_2 of poly-ZnSe [36] (solid left pointing green triangles), *p*-ZnSe at 1270 nm (solid blue triangles [33]), from [25] (solid orange diamonds), from [37] (solid red star) and n_2 as measured in our experiment (solid black square) at

 $\lambda_{\rm MIR} = 3.9 \,\mu m$

4.5 Simulation results

We have simulated optical propagation and filamentation with the ultra-short pulse at $\lambda = 3.8 \mu$ m and the focus geometry matching that in the experiment. There was freedom to choose the best effective second order nonlinearity d_{eff} , as a range of values from 16 to 132 pm/V was found in the literature [38,39]. Varying the initial peak intensity of the pulse, we sample the pulse energies in the range 0.8-8.6 μ J. Because the simulation runs with different realizations of the random "disorder" embodied in r(z), giving rise to spectra with significant noise, we perform spectrum averages over four realizations, and smooth the resulting spectra.

Figure 11 shows representative results for the harmonic generation and inter-harmonic continuum evolution. Figure 11(a) illustrates the evolution of the spectrum, here shown between harmonic orders three to seven, versus the propagation distance. One can see that the harmonic orders gain significant energy almost immediately after the pulse enters the sample. On the other hand, it takes a certain propagation distance for the supercontinuum to fill in the "valleys" between harmonic orders.

Figure 11(b) depicts the simulated spectra for a range of initial pulse energies. As the pulse energy increases, strong harmonic generation is accompanied by supercontinuum generation eventually resulting in significant energy density spanning the whole interval of 0.5 μ m – 4 μ m. The behavior of the spectra is qualitatively like that seen in the experiment, although the distinct harmonic orders decrease somewhat faster and the spectral "valleys" are slightly deeper.

The simulated spectra exhibited the blue-shift observed experimentally, the effect mostly being mediated by the free carrier (FC) density changes. The intensity dependent FC generation in mid-IR wavelengths was incorporated from previous works on ZnSe and other materials described elsewhere [40,41]. Over the range of initial pulse energies from 0.2 to 7.1 μ J the third-harmonic spectral peak shifts by ~ 20 nm. By varying various parameters in our simulations, we find that the blue-shift is mainly controlled by the free carrier generation. There is high conversion efficiency from the fundamental into new spectral components. The simulations show up to twenty percent of the energy can be converted already in the single-filament regimes simulated here.



Fig. 11. Simulation results for harmonic and supercontinuum spectrum generation in ZnSe. (a) Spectra at two different propagation distances in the sample for a pulse with the initial energy of 7.1 μ J. (b) Spectra at propagation distance z = 10 mm for a range of pulse energies between 0.8 and 7.1 μ J.

4.6 Simulation insights

To the best of our knowledge, ours is the first space- and time-resolved simulation of the extreme spectral dynamics in poly-ZnSe samples. While we have utilized a simplified model, treating the second-order nonlinearity as an effective scalar medium, it is fair to say that the simulation outcomes are in qualitative agreement with the experiment. This encourages us to draw insights from our modeling.



Fig. 12. Spectral broadening in the vicinity of the fundamental frequency. Side-bands develop with increasing pulse energy due to SPM, while the asymmetry of the spectrum is likely due to carrier-induced blue shift.

The simulation results illustrate (Fig. 12) the spectral broadening in the vicinity of the initial fundamental MIR driver pulse propagating through poly-ZnSe, and may be compared with the experimental spectrum in Fig. 6(b). The qualitative comparison between the simulation and experiment is quite good, especially on the short-wavelength side of the

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fundamental, where the wavelengths corresponding to the spectral side-band and the minimum at $3.7 \mu m$ are nicely reproduced. The spectral broadening on the long-wavelength side also exhibits a band similar to that in the experimental data, though at a lower relative strength. Given the effective nature of the model employed in this work we find this result encouraging.



Fig. 13. Temporal and spectral properties of the electric field for a single random poly-crystal realization. (a) Temporal waveform of the real electric field exhibits a strong presence of higher-harmonic components which concentrate predominantly in the long tail of the resulting composite pulse. The inset zooms on the electric field profile near the peak, revealing that harmonics and fundamental together give rise to a "random" waveform with non-sinusoidal oscillations. (b) The corresponding spectrum shows that harmonic orders (marked by labels) show increasing levels of noise.

The simulations also reveal several mechanisms that contribute to the harmonic generation that looks very much non-perturbative in the sense that the decrease of the energy in the higher orders is very slow. The first important aspect is that several "paths" of different frequency combinations contribute to any given harmonic order. For example, third harmonic receives second-order contribution from the sum of the fundamental and second harmonic. At the same time, third-order nonlinearity generates third harmonic directly. Other ways to produce this frequency include frequency difference process, such as subtracting the fundamental from harmonic order four. All these processes end up with slightly different phase relations and this decreases the temporal coherence of the resulting multi-color waveform, which in turn is less likely to feed the energy back into the fundamental.

In order to elucidate these conclusions, we show in Fig. 13(a) an example of the electricfield waveform as it evolved over 10 mm propagation in a sample without averaging, over several random realizations of the orientation of crystallites (as was done for the simulation of harmonic spectra shown in Fig. 11). The feature that indicates the loss of coherence is the long tail that consists mainly of the higher-frequency waves, together with the essentially random local structure of the waveform. The latter is illustrated in the inset which zooms onto the peak region—here one can appreciate that the superposition of different spectral components appears random, which in turn is an indicator of incomplete coherence. The large temporal extent of this composite pulse is another reason why the energy from the upper spectral bands cannot be effectively returned to the fundamental, a mechanism that underlines the efficiency of the random quasi-phase-matching.

Figure 13(b) adds to this argument, showing that the spectrum also exhibits random noisy fluctuation that arise due to superposition of waves with poorly correlated mutual phases. It is also obvious that the random noise becomes more and more evident in higher harmonic

orders, which is in line with many more channels (i.e. combinations of other harmonics) that contribute to them.

The second important aspect is the random quasi-phase-matching due to the randomness of the grain orientation. In our treatment, this leads to random on/off in the second-order processes that in turn destroy the coherence required for the energy to flow back to the fundamental.

The third mechanism that needs to be recognized is the group-walkoff between different spectral components. Because of greatly varying group velocities between different orders, the high-frequency components lag behind the main pulse and thus have little opportunity to return their energy back into fundamental.

Finally, free electron generation contributes in two ways. First, it is the spatial and temporal defocusing adding yet more randomness and subsequent loss of coherence. Second, the fast-increasing electron density imparts blue shift and contributes significantly to spectral broadening of all components, thus opening more and more channels for spectral conversions.

Of course, one possibly important aspect that has not been considered in our modeling is that grain boundaries can also add to phase mismatch as they probably appear like locally single-axis anisotropic medium. A fully resolved vectoral model with "microscopic" modeling of the poly-crystalline nature of the medium is needed to test if grain boundaries contribute in significant ways. Such an investigation is left for a future work.

5. Conclusion

Ultrafast MIR nonlinear optics is an exciting new field, and much interest has been recently shown in RQPM of polycrystalline materials due to promising applications to SC generation and ultra-broadband HHG. This paper has investigated HHG and SC generation in poly-ZnSe using MIR pulses of two different wavelengths, two focal geometries, and for an array of input pulse powers and propagation lengths. Under these conditions it was shown that IHC can be generated with harmonics out to 7th order without significant broadening in the fundamental. Harmonics generated this way were found to exhibit non-perturbative scaling laws for all harmonic orders. We found that longer propagation lengths lead to stronger nonperturbative behavior. Spectral broadening of the fundamental could be achieved by increasing the propagation distance (with a fixed pulse power) instead of increasing the intensity due to RQPM. The RQPM nature of the interaction was further confirmed by the observation of linear scaling in the harmonic efficiency with propagation length, as well as by high conversion efficiency (36%). With the same pulse power, broadband SC generation could be induced by using a tighter focus, high intensity setup. Blueshifts observed in the harmonics could possibly be explained by photon acceleration [21], although further study would be needed. We also compared harmonics generated in poly-ZnSe to those generated in single crystal ZnSe and found single crystal ZnSe to have more than an order of magnitude lower harmonic efficiency, and an absence of harmonics beyond the 3rd. The threshold for multiple filamentation in terms of both pump power and propagation distance was extracted for our conditions. It was demonstrated that IHC comes primarily from filamentation within the material. Z-scans were performed to determine n, experimentally for a MIR wavelength, showing good agreement to the existing theory. Z-scan results were used as an input for numerical modeling of filamentation in poly-ZnSe. Our simulations show good qualitative agreement with the experiments and have led to insights about the underlying physics.

Funding

SURVICE (S17-095008/DOTC-17-01-INIT0086); Air Force Office of Scientific Research (AFOSR) (FA9550-16-1-0069); AFOSR multidisciplinary research program of the university research initiative (MURI) (FA9550-16-1-0013); AFOSR (FA9550-16-1-0121); AFOSR (FA9550-16-1-0088).

Disclosures

The authors declare that there are no conflicts of interest related to this article.

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