

# PROPERTIES OF SECOND HARMONIC AND SUM FREQUENCY GENERATION IN POLYCRISTALLINE ZnSe

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**Abstract.** The second harmonic generation (SHG) and sum frequency generation (SFG) of polycrystalline ZnSe were studied in a femtosecond time scale. Beside SHG and SFG dot patterns in polycrystalline ZnSe we found SFG ring pattern and the optimal orientation of the ZnSe crystal to obtain SFG ring pattern. We also discovered the dispersion and the spectral broadening of the SH dot pattern by self-phase-modulation effect. Studies of the SH dots patterns of several polycrystalline ZnSe samples showed a characteristic SH dot pattern for each sample.

**Key words:** Optical parametric amplifier (OPA), Second harmonic generation (SHG), Sum frequency generation (SFG), Optical Kerr effect, Self-phase-modulation, birefringent crystals, degenerate four-wave mixing (DFWM), Group Velocity Dispersion, pump - probe method

## 1. Introduction

ZnSe is one of II-VI semiconductors which have attracted much interest in view of the potential for optoelectronic applications. Polycrystalline ZnSe is also used as an IR-transmission material to make IR -lens, windows...and is a new medium promising for autocorrelation measurement of ultra short laser pulses [1].

Among several semiconductor materials of zincblend structure, ZnSe shows a high nonlinear optical coefficient. The optical nonlinear properties such as SHG, SFG ...in single-crystalline ZnSe were well known in nanosecond or picosecond time scale but not much reported yet in femtosecond time scale with polycrystalline ZnSe samples. When using high peak power tunable femtosecond laser beams to study the nonlinear optical properties of ZnSe polycrystals we found sum frequency generation (SFG) and second harmonic generation (SHG) in form of dots pattern which superficially look like the Laue patterns in X-ray diffraction [2,3]. Several experiments were carried out to study the nature of these dot patterns. During a study of SFG dot patterns in polycrystalline ZnSe samples by the non-collinear laser beams we have additionally observed SFG in the form of ring patterns when changing the orientation of the sample.

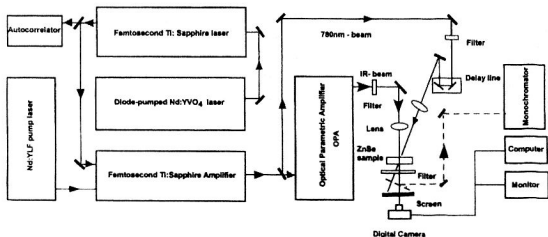
Second harmonic generation in singlecrystalline semiconductor materials of point group 43m structure such as ZnSe is well known. There is not exact phase matching in these materials because they are not birefringent and their dispersion is normal. However, our experiments showed SFG and SHG ring patterns in single-crystalline and polycrystalline ZnSe like the well known SHG ring patterns in birefringent uniaxial crystals.

This experimental result drew our attention to the change of refractive index of ZnSe crystal under the influence of the intense femtosecond laser pulses (Optical Kerr effect)

More experiments were carried out to study the nature of the SH ring and dots patterns in ZnSe material and reported in this paper.

## 2. Experimental setup

The experimental setup is shown in the figure 1. The optical parametric amplifier (OPA-800, Spectra Physics) is pumped by 780 nm wavelength beam from the Ti: sapphire amplifier and generates laser pulses of 130 fs duration, 1 KHz repetition rate and an energy up to 45  $\mu$ J. The wavelength of the OPA output beams is tunable from 1.1 to 2.2  $\mu$ m and the polarisation of these beams is linear. Sum frequency generation is carried out in ZnSe sample by 780nm -beam splitted from the femtosecond Ti:sapphire amplifier output and tunable IR-beam from OPA. The angle between these two fundamental beams is  $14^\circ$ . A delay line was used to overlap the pulses of the two fundamental beams in ZnSe sample. The ZnSe sample is mounted in a special holder so that it can be rotated around two axis: one axis is normal to the page of the figure 1 (vertical axis) and the other one is on the page and perpendicular to the IR beam direction (horizontal axis). The dot and ring patterns were observed on a semitransparent white screen 3cm behind ZnSe sample and taken by a digital camera (Nikon, Coolpix 990). The wavelengths of SFG and SHG radiation were measured by a monochromator. The polycrystalline ZnSe sample manufactured by "EKsMA" has a thickness of 3mm. The single-crystalline ZnSe sample manufactured by "MaTec K" has orientation (111) and a dimension of  $10 \times 10 \times 2$  mm<sup>3</sup>. Both of them have polished surfaces.



*Fig 1.* Experimental setup: The mode-locked Ti:sapphire laser (Tsunami, Spectra-physics) is pumped by the diode-pumped, CW-NdYVO4 laser (Millenia, Spectra-Physics). The OPA (OPA-800 Spectra-Physics) can give a range of pulses with wavelengths from 1100 to 2600nm and a repetition rate of 1 KHz. The laser beams are focused on the ZnSe sample mounted on a rotatable holder (not in the focus point)

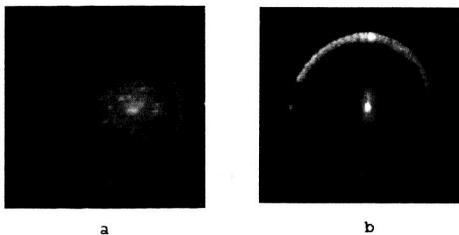
### 3. Results and discussion about the ring pattern

When using non-collinear fundamental beams as shown in fig.1 and changing the orientation of the polycrystalline ZnSe sample we found SFG in form of ring pattern beside SFG dot pattern( Fig.2a) In the fig 2a , the SFG ring and dot pattern was created by 780nm and 2114nm beams and has a yellow -green colour with the measured wavelength of 569nm .

The SFG dots and ring patterns appear only when the femtosecond pulses of the two fundamental beams are overlapped by delay line.

In order to study the nature of these SFG rings, we replaced the polycrystalline ZnSe sample by the single-crystalline ZnSe sample and used two collinear fundamental beams.

For simplicity, we studied the SHG ring patterns. As we expected, in a suitable orientation of the single-crystalline ZnSe , the SHG ring pattern (red-618nm) by 1236nm beam appeared ( fig.2b).



*Fig 2. 2a.* SFG ring and dot pattern (yellow – green) in polycrystalline ZnSe sample by 780nm and 2114nm beams; *2b.* SHG ring pattern in single-crystalline ZnSe sample by 1236 nm beams

The optimal orientation of the crystal was obtained when the crystal was rotated  $15^\circ$  around the vertical axis from the initial position where the input laser beam is perpendicular to the crystal surface. The half -angle of the cone formed by the red ring and the output point on ZnSe surface is  $22^\circ$ . These rings appear within about 6 degrees around the optimal orientation. This optimal orientation depends not only on the orientation of the crystal with laser beam direction but also on the angle between electric field of input laser beam and the normal of the crystal surface.

With the optimal orientation, the appearance of SFG and SHG rings depend strongly on the intensity of the fundamental laser beams. The SFG and SHG rings appear only when the laser power is larger than a determined value.

According to the experimental observations we assume that under the influence of the intense femtosecond laser pulses, the refractive index of ZnSe crystal changes. As we know, isotropic samples (liquids or glasses) become anisotropic (birefringent) under the action of an applied electric field (Kerr effect). The electric field associated with an intense linearly polarized light pulse induces the Kerr effect (optical Kerr effect). The samples take on the characteristics of an uniaxial crystal whose optic axis corresponds to the direction of the applied field  $E$ .

In the crystals which have not inversion symmetry like ZnSe, the situation is considerably more complicated. The change of refractive index depends on the orientation of crystal structure with the electric field. The refractive index of ZnSe sample becomes to be not the same in every direction and ZnSe crystal shows SHG ring patterns like birefringent crystals. The change of refractive index is of the quadratic electro-optic effect, so the SFG and SHG ring appearance depends strongly on laser input intensity.

Our experimental results support that the intense femtosecond laser pulses may enhance the anisotropy or change the crystal symmetry by nonlinear interaction and result in the SHG ring patterns

#### 4. Results and discussion about dot pattern

To study the dot pattern, the experimental set up was arranged as shown in the fig. 3. For simplicity, we studied only SHG dot pattern. The fundamental beam which is the signal light from OPA (OPA-800 Spectra Physics) is directed perpendicularly on the ZnSe surface. The polycrystalline ZnSe sample has a thickness of 3mm. Both of the front and back surfaces of the sample are polished. The SHG dot pattern were observed on a semitransparent white screen 7cm behind ZnSe sample by a digital camera. A convergent lens is mounted on a translatable holder so that the lens can be translated along the fundamental beam direction.

The SHG dot pattern was obtained without the convergent lens  $L$  and shown in the figure 4a. Using a convergent lens in a relevant distance from the sample we found a clear dispersion of the SH dots on the screen and the number of SH dots decreased in comparison with the above case (fig.4b). In the dispersion, the color of the SH dots is red-shifted inside and blue-shifted outside. We measured the wavelengths of the SH dots by a monochromator and found a spectral broadening and a blue-shift of the central wavelength. (table 1)

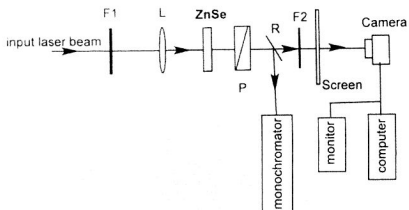


Fig 3. The input laser beam comes from the OPA (OPA – 800 spectra physics) the convergent lens ( $f=19\text{cm}$ ) is mounted on a translated holder; F1,F2 – filters; P – polarizer; R – output reflector

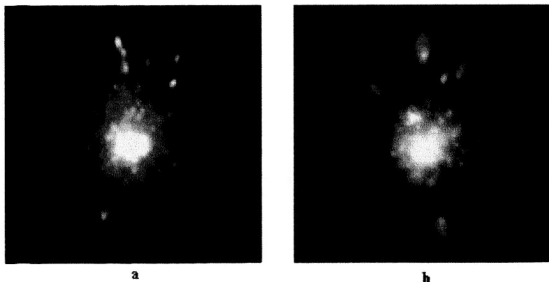


Fig 4. The SHG dot patterns in polycrystalline ZnSe sample; a – The SHG dots pattern obtained without a focusing lens; b - The SHG dots pattern obtained with a focusing lens; The focus length is 19cm, the distance from the lens to the sample is 21cm; The wavelength of the fundamental beam is 1156nm.

Table 1: The spectral broadening and the blue-shifting of the SH dots. The focus length of the lens is  $f = 19\text{cm}$  and the distance of the lens from the ZnSe sample is  $d = 21\text{cm}$ .

	Peak wavelength	Spectrum
Without lens	578nm	567-588nm
With lens $f = 19\text{cm}; d = 21\text{cm}$	567nm	546-593nm

This result showed that the nature of the dot pattern is neither an interference nor a degenerate four-wave mixing (DFWM) effect in which the long wavelength has a larger diffraction angle than the short one in the same interference order. In fact, we observed a dispersion of the SH dots in which the colour of dots is red-shifted inside and blue-shifted outside.

The spectral broadening and the blue-shift of the central wavelength of the SH dots are explained by the self-phase-modulation. In the femtosecond time scale, under the interaction of intense Gaussian light pulses, the nonlinear index of material can be expressed as

$$n = n_0 + n_2 \cdot I(t) / 2 \quad \text{with } I(t) = \exp(-g \cdot t^2). \quad (1)$$

For the sake of simplicity we consider a plane wave propagating in the nonlinear material.

$$E(t, x) = E_0 \exp \{i(\omega t - kx)\}; \quad k = \omega_0 n(t) / c \quad (2)$$

The instantaneous frequency can be written as

$$\omega(t) = \partial \Phi(t) / \partial t = \omega_0 + \omega_0 n_2 x [ \partial n(t) / \partial t ] / c \quad (3)$$

and the frequency variation as

$$\partial \omega(t) = \omega(t) - \omega_0 = -\omega_0 n_2 x [ \partial I(t) / \partial t ] / 2c \quad (4)$$

In the process named self-phase-modulation, according to (4) if  $n_2$  is positive, new low frequencies are created in the leading edge of the pulse envelope and new high frequencies are created in the trailing edge (figure 5). The self-phase-modulation leads to a spectral broadening of the laser pulse.[4,6,7] Induced index variations can also be observed in pump and probe experiments. An intense pump pulse can induce an index change in a medium, which can be experienced by a weak probe pulse. In the time domain the dynamical index change created by the pump shifts the central frequency of the probe. With positive  $n_2$ , the probe frequency is red-shifted when it leads the pump and is blue-shifted when it trails the pump. In the space domain the probe beam undergoes focusing or defocusing as well as deflection depending on the relative geometry of the pump and the probe beams[4].

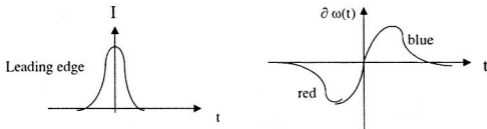


Fig.5. a-Intensity dynamics of a Gaussian laser pulse

b-Time-dependence of  $\partial \omega(t)$  and the central frequency  $\omega(t) = \omega_0 + \partial \omega(t)$

In our experiments the IR-fundamental pulse played the role of a pump and the visible SH pulse played the role of a probe. Because the wavelength of the fundamental pulse is longer than the SH pulse (double frequency), the fundamental frequency has a higher velocity and leads the SH pulse (Group Velocity Dispersion).

That why the central wavelength of SH dots was blue-shifted (table 1) and their spectrum was broadened when using a convergent lens. In the space domain, the fundamental pulse causes a deflection of the SH pulse by the induced index variation that results to the SH dot pattern.

Keeping the lens position in a determined distance we observed the SH dot patterns with four different samples of polycrystalline ZnSe made in Lithuania, Germany, USA...The samples were placed perpendicularly to the fundamental beam direction in the same position. Each sample gave a characteristic SHG dot pattern. The polarisation status of the SH dots was also observed by an analyser placed behind one of the ZnSe samples. When rotating the analyser around the fundamental beam direction some groups of SH dots disappear. This result showed that each group of SH dots has its own polarisation status.

We replaced the polycrystalline ZnSe sample by the single-crystalline ZnSe sample with orientation [111] and then [100] and repeated the experiments and observed that the SH dot pattern did not appear in any position of the lens, in any position of the incident point on the ZnSe surface and in any rotation of the sample. The fact that the SH dots appear only in the polycrystalline ZnSe samples shows that the SH dot pattern has origine from the polycrystalline structure.

In microstructure, the polycrystalline ZnSe material consists of many tiny monocrystals. For ZnSe, the sizes of all small monocrystals are approximately identical due to the CVD (Chemical Vapor Deposition) as manufacturing process and they are 50-70 $\mu\text{m}$  [1].

The calculated coherence length  $l_c$  for SHG of singlecrystalline ZnSe is 126 $\mu\text{m}$ [2]. Because the sizes of all small monocrystals are shorter than the coherence length they all could give SHG and contribute to the total SHG only depending on their orientation. Several experimental results showed that the SHG output signal in a monocrystal of the point group  $\bar{4}3m$  like ZnSe depends on the orientation of these monocrystals vs the electric field of the fundamental beam [1,8]. Because the orientations of the tiny monocrystals within the polycrystalline ZnSe material are random, a monocrystal grain may be able to generate SH while its neighbours may be not and some groups of the tiny monocrystals of the suitable orientation can generate SH signal more intense than the others. The SH light generated in a group of tiny monocrystals with the same orientation has the same polarisation status.

The SH signal generated in a small monocrystal with the optimal orientation has the intensity stronger than the others and during its propagation in nonlinear medium this SH signal undergoes a deflection due to the induced-index variation by the fundamental pulse. The induced -index variation takes place with different levels in the small monocrystals of different orientations and results in the inhomogeneities of refractive index within the polycrystalline ZnSe material. The crystal defects if available by manufacturing will enhance this process [7,9]. The SH pulse which trails the fundamental pulse undergoes deflection, refraction, dispersion and spectral broadening... The SH dot patterns observed in our experiments reflected all these effects. The polycrystalline ZnSe samples formed by

many small monocrystals with different orientations and crystal inhomogeneities due to manufacturing process give the characteristic SH dot patterns

In the femtosecond time scale, we can observe the SH dot pattern without a convergent lens if the laser pulse is intensive enough. When using a lens to focus the laser beam on the ZnSe sample the above effects which are proportional with the light intensity were enhanced but the number of dots decreased because the number of tiny monocrystals in the volume excited is smaller

## 5. Conclusion

The SHG and SFG ring pattern was found beside the dot pattern. The dispersion and spectral broadening by self-phase modulation of the SH dots were also discovered. Our experimental results led to an explanation of SHG dots and ring pattern and suggested that the SHG dot pattern could be used to distinguish the different ZnSe polycrystalline samples and give some information about the inhomogeneity of these samples.

The SHG and SFG in form of the dot and ring patterns come from a nonlinear interaction inside the ZnSe crystalline structure. The intense femtosecond laser pulses may enhance the anisotropy and the inhomogeneity of crystals by induced -refraction index variation.

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