1 Third Harmonic Generation from composite $FAPbBr_3$ nanocrystal film

An excitation laser source (Yb:KGW PHAROS laser system) with 200 fs pulses and 100 KHz repetition rate is pumping an optical parametric amplifier (Pharos, Light-Conversion), producing pulses with energy of 0.5-1 μJ, tunable between 1340 nm to 1740 nm. The third harmonic generation (THG) from the FAPbBr3 nanocrystals film is excited at normal incidence by focusing the pump laser down to a ~ 68 micrometer (FWHM) spot, using a 400 mm lens. The third-harmonic signal in the transmission direction is coupled into a multi-mode fiber spectrometer (Flame, Ocean Optics) after collimation and refocusing using a telescope system of 200 mm + 12 mm lens or into a power-meter for measurements of absolute efficiency. The pump beam is filtered out of the collection using a bandpass filter with 80% transmission in the wavelength range 400 nm - 650 nm.

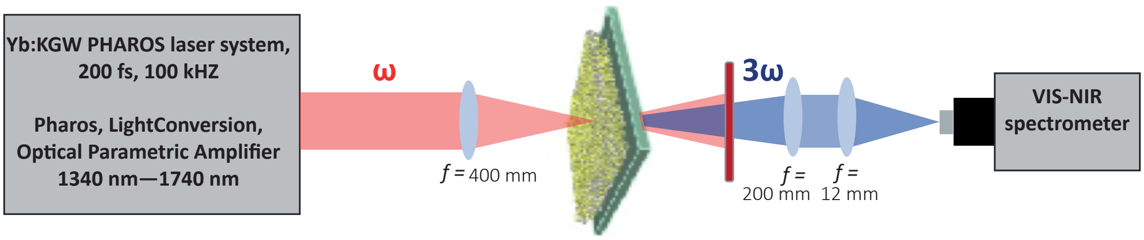

Figure 1: **Experimental Schematic**. (a) Scheme of the third harmonic generation experiment from composite $FAPbBr_3$ nanocrystal film.

2 Extracting the third-order nonlinear susceptibility of composite $FAPbBr_3$ nanocrystal film

Our aim is to extract the third-order nonlinear susceptibility of the 1300nm composite $FAPbBr_3$ nanocrystal film composed of silica, air and $FAPbBr_3$ nanocrystals.

We present here the expression used to predict the intensity of the generated third harmonic, $I_3(\lambda)$, from a thin film, as presented in Eq. (1). This is an analytical solution to the nonlinear Maxwell's equations assuming a non-depleting pump wave in a sufficiently thin film [1].

$$I_3(\lambda) = \frac{9\omega_1^2 L^2}{16 \mid \widetilde{n_3} \mid n_1^3 \epsilon_0^2 c^4} \mid \chi^{(3)} \mid ^2 I_1^3 (\frac{e^{-2\alpha_3 L} - 2cos(\Delta k L) e^{-\alpha_3 L} + 1}{\alpha_3^2 L^2 + k_3^2 L^2}) e^{-2\alpha_3 L} \tag{1}$$

Where the absorption coefficient, $\alpha_3 = \frac{2\pi\kappa_3}{\lambda_3}$, is dependent upon the extinction coefficient, κ_3, at the third harmonic wavelength, λ_3. The phase mismatch between the pump and the third harmonic wave, $\Delta k = \frac{6\pi(n_1 - n_3)}{\lambda_1}$, is dependent upon the real part of the refractive index at the pump wavelength, n_1, and third harmonic wavelength, n_3, and the pump wavelength, λ_1. The length of the sample is defined by L. In Eq. (1), I_1 is the pump intensity, the third-order nonlinear susceptibility is $\chi^{(3)}$, the angular frequency of the pump is ω_1, and the complete refractive index at the third harmonic wavelength is $\mid \widetilde{n_3} \mid$. The physical constants, ϵ_0 and c maintain their usual definitions. We write Eq. (1) in the following form:

$$I_3(\lambda) = \mid \chi^{(3)} \mid ^2 I_1^3 f(\lambda) \tag{2}$$

Where the function $f(\lambda)$ is

$$f(\lambda) = \frac{9\omega_1^2 L^2}{16 \mid \widetilde{n_3} \mid n_1^3 \epsilon_0^2 c^4} (\frac{e^{-2\alpha_3 L} - 2cos(\Delta k L) e^{-\alpha_3 L} + 1}{\alpha_3^2 L^2 + k_3^2 L^2}) e^{-2\alpha_3 L} \tag{3}$$

We compute the function $f(\lambda)$ for the composite $FAPbBr_3$ nanocrystal film and microscope glass slide, defined as the $f^{composite}(\lambda)$ and $f^{glass}(\lambda)$ respectively, at wavelengths

between 1340-1740 nm in increments of 20 nm.

We use the linear optical properties of the composite $FAPbBr_3$ nanocrystal film obtained from ballistic transmittance and specular reflectance measurements at different incidence angles as described in the main text to compute $f^{composite}(\lambda)$ and the optical linear properties of the microscope glass slide presented in [2] to compute $f^{glass}(\lambda)$.

From Eq. (2) it is clear that the computation of $f^{composite}(\lambda)$ and $f^{glass}(\lambda)$ can be used alongside the corresponding experimentally measured THG intensity for the composite $FAPbBr_3$ nanocrystal film and glass, $I_3^{composite}$ and I_3^{glass} respectively, at wavelengths between 1340-1740 nm, to calculate the third-order nonlinear susceptibility of the composite $FAPbBr_3$ nanocrystal film, $\mid \chi^{(3)composite}(\lambda) \mid$. This is shown in Eq.(4). The fluctuations of the pump intensity, I_1 due to differences in spectral beam diameter, as shown in Eq.(2), is factored out by taking the ratio with the measurements/calculations from the reference glass microscope slide, which is spectrally flat [3], where the pump intensity is experimentally delivered in the same way as the composite $FAPbBr_3$ nanocrystal film.

$$\mid \chi^{(3)composite}(\lambda) \mid = \mid \chi^{(3)glass} \mid \left(\frac{I_3^{composite}}{I_3^{glass}} \frac{f^{glass}(\lambda)}{f^{composite}(\lambda)}\right)^{1/2} \quad (4)$$

Where $\mid \chi^{(3)glass)}(\lambda) \mid$ is the third-order nonlinear susceptibility of the microscope glass slide and has a spectrally flat value is $\mid \chi^{(3)glass} \mid$ = (1.6 ± 0.2) x 10^{-22} m^2/V^2 [4].

Correcting for the volume contribution to extract third-order susceptibility of $FAPbBr_3$ nanocrystals

Through Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES), the percentage of volume encapsulated by $FAPbBr_3$ nanocrystal is determined to be is 6.5 ± 0.1%, and the remaining 50% and 43.5% is made up of SiO_2 and air respectively.

We correct for the volume contribution (filling fraction, ff)from each constituent part of the composite nanocrystal film and report the final third-order nonlinear suscepti-

bility of the $FAPbBr_3$ nanocrystals, $\mid \chi^{(3)NC)}(\lambda) \mid$ as:

$$\mid \chi^{(3)NC}(\lambda) \mid = \frac{\mid \chi^{(3)composite}(\lambda) \mid}{ff_{NC}} \tag{5}$$

Where $ff_{NC} = 0.065$. We have assumed that the third-order nonlinear susceptibility is much greater for the $FAPbBr_3$ nanocrystals than the remaining SiO_2 and air constituents of the composite thin film.

Eq. (5) allows us to extract spectral response of the third-order nonlinear susceptibility of the $FAPbBr_3$ nanocrystals.

References

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