Self-quenching effects of excitons in $CaWO_4$ under high density XUV FEL excitation

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Using free electron laser excitation in the XUV range, $CaWO_4$ samples were exposed to ultra-short, intense photon pulses (photon energy 89.84 eV, 10 μJ average pulse energy, 25 fs pulse length), and their luminescence was studied with time-resolved spectroscopy. In the decay curves measured in the temperature range 8–300 K, a non-exponential emission decay with shortening of the life times over the first few μs is observed, which depends on the excitation density. Using a model for dipole–dipole interaction of excitons under non-uniform excitation densities, the structure of the decay curves can be reproduced in good agreement with the experimental data, and parameters for the initial exciton interaction can be calculated.

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1. Introduction

In the last few years, new sources for highly intense, ultrashort laser pulses with photon energies in the vacuum and extreme ultraviolet (VOV and XUV) range, based on free electron lasers (FEL), have been developed. The first FEL of this kind to provide beam for interested scientists is the FLASH facility of DESY in Hamburg [1]. In addition, several other FELs operating at photon energies from the VUV to the soft X-ray region are in the planning phase or under construction elsewhere. Also, a joint European X-ray FEL source, which will provide intense coherent X-ray pulses of femtosecond duration, will be built at DESY, and it is scheduled to be operational in 2013.

With the development of these new sources, new challenges appear also in the field of material science. The photon densities of a XUV FEL are close to the expected damage thresholds of the materials used as optical elements for the FEL radiation, and extensive research was directed in the last years to investigate their durability under these conditions [2,3]. Aside from the problem of radiation-induced damage of the optical components, the performance and stability of materials used for the detection of radiation needs to be investigated. Scintillators are already now widely used to monitor and tune the performance of the FEL at FLASH [4], and future experiments at the XFEL may rely strongly on the performance of scintillators and visualization screens under the intense X-ray excitation.

First experiments were carried out during the test phase for the currently operating FLASH FEL for various samples using pulses with 13.9 eV photon energy, and a distinct change in the decay behavior was observed [5]. Due to time constraints, many questions raised as a result of the experiments remain open. With the FLASH laser now in operation, we had the chance to investigate various scintillator materials in more detail.

In this work, we focus on luminescence from $CaWO_4$ crystals. Renewed interest to tungstate crystals as scintillator materials has appeared in the last decades due to their radiation hardness and the occurrence of fast (a few ns in $PbWO_4$) intrinsic emission bands [6–8]. The intrinsic nature of these luminescence bands allows the application of a model for self-quenching due to exciton–exciton interaction outlines in [9].

2. Experimental

The measurements were performed at the BL1 beamline of the XUV free electron laser facility FLASH of DESY in Hamburg, Germany. This unique facility provides ultrashort laser pulses (25 fs), the photon energy used in experiments was 89.84 eV. The circular spot size on our samples was about 150 μm in diameter. The pulse energy of the FEL varies statistically from pulse to pulse due to the stochastic process of self-amplification by spontaneous emission [1]. In addition to this inherent distribution of pulse energies, a N_2 gas attenuator in the beamline with controllable pressure was used to reduce the average FEL beam intensities over a range from 10 to 100% compared to the unattenuated beam. The maximum values for the peak energies were about 25 μJ; this corresponds to $1.7 \cdot 10^{12}$ photons per pulse for the given photon energy. The polished single crystal sample of $CaWO_4$ was glued on the cold finger of a He cryostat prior to mounting in a UHV

experimental chamber. Measurements were performed at $T = 8$ and 300 K.

Luminescence for the decay spectra was detected using a XP2020Q photomultiplier in combination with suitable band-pass filters to select the desired emission range. Decay curves were recorded as single shot measurements for each FEL pulse using a fast digital oscilloscope. A reference signal from a microchannel plate detector in the beamline monitoring the FEL intensity for each pulse was recorded simultaneously with the decay to allow precise comparison of the measured data. The values for the pulse energies used throughout this work were obtained through linear regression from the pulse energies recorded in the database of FLASH and the measured beamline detector signals. To reduce the noise level of the recorded single-shot decay curves, decay curves were sorted according to the measured pulse intensities and averaged over 10% intervals of the full pulse energy range.

In addition to the decay measurements, also luminescence spectra for the samples were recorded using an ARC SP308i UV/visible spectrograph equipped with a Princeton Instrument CCD detector. The emission spectra were averaged over 2000 FEL pulses, and the average intensity was adjusted by changing the transmission of the gas attenuator.

3. Results and discussion

Luminescence spectra for $CaWO_4$ under 89.84 eV FEL excitation are shown in Fig. 1 for temperatures of 8 and 300 K and different attenuation levels of the FEL. The average pulse energy of the unattenuated radiation is approximately 12 μJ for both temperatures. In the spectra, two well-known emission structures are observed. The strong luminescence band peaking at approximately 450 nm is ascribed to excited WO_4^{2-} centres forming molecular self-trapped excitons (STE) [10], whereas the broader and weaker emission bands at longer wavelength above ~ 550 nm originate from impurity/defect centres in the crystal. In both low and room temperature spectra, this long wavelength tail is suppressed for higher photon fluences. Two different mechanisms can be responsible for this behavior: 1) a higher probability of electron-hole recombination and exciton formation at increased intensities, reducing the probability of energy transport to defect centres by free carriers, and 2) saturation of the impurity/defect centres which limits the possible luminescence yield for this type of emission.

Decay spectra of $CaWO_4$ for different averaged FEL pulse energies are shown in Fig. 2 for sample temperatures of 8 and 300 K. In the initial part of the decay spectra, a strong non-exponential behavior is observed, whereas for decay times larger than ~ 5 ns, the decay can be approximated by a single-exponential curve with a radiative life-time τ_r comparable to results obtained with low-density excitation [6,10]. The initial non-exponential decay becomes more pronounced with increasing pulse energies, indicating a direct influence of the excitation density on the radiative life-time of the STE states in the crystal.

To understand this effect in more detail, we analyzed the data using the model of bimolecular self-quenching of STE under non-uniform excitation densities, which considers energy transfer between two STEs situated at small distance R due to dipole–dipole interaction. One exciton recombines (non-radiatively or under emission of a virtual photon), and its energy is transferred to the second STE, which becomes excited or ionized to form a free electron-hole pair. Since exciton formation is the prevalent mechanism for relaxation from these excited states, we can assume that, after a relaxation process within some picoseconds, the result of the energy transfer is a single STE. For this process of the type $\mathrm{STE} + \mathrm{STE} \rightarrow \mathrm{STE}$, we can formulate a rate equation for the spatial exciton density $n(\mathbf{r}, t)$ in the form

$$\frac{\partial n(\mathbf{r}, t)}{\partial t} = -\frac{n(\mathbf{r}, t)}{\tau_r} - \gamma(t, \mathbf{r})\, n^2(\mathbf{r}, t), \tag{1}$$

with the bimolecular rate of reaction $\gamma(t, \mathbf{r})$. In the simplest form this rate can be expressed as

$$\gamma(t, \mathbf{r}) \equiv \gamma(t) = \frac{q_{\mathrm{d-d}}}{2} \frac{R_{\mathrm{d-d}}^3}{\sqrt{t\tau_r}}, \quad q_{\mathrm{d-d}} = \frac{4\pi^{3/2}}{3} = 7.42, \tag{2}$$

where we use the dipole–dipole transfer radius $R_{\mathrm{d-d}}$ [9]. Note that Eq. (2) does not depend on $\mathbf{r}$, because we can expect that any spatial correlation of excitons due to initial creation or diffusion during their lifetime τ_r occurs on a much larger scale than the transfer radius $R_{\mathrm{d-d}}$.

The initial concentration of the excitons due to absorption of the FEL pulse in the crystal can be approximated by a Gaussian radial distribution in the plane of the sample surface and an exponential decrease along the crystal depth z with the absorption coefficient α. Thus, we formulate the initial STE density as

$$n(\rho, z, 0) = I_0 \frac{\alpha\sigma}{\pi a^2} e^{-\rho^2/a^2 - \alpha z}, \tag{3}$$

where ρ is the radial coordinate on the surface, a is the FEL spot radius, I_0 the total number of photons in a pulse, and σ is the excitation yield (number of excitons created per incident photon). With this initial condition $n(\mathbf{r}, 0)$, we can solve the rate equation (1) to obtain the expression for the decay intensity in the form

$$I_{\mathrm{lum}}(t) = \frac{\sigma I_0}{\tau_r} e^{-t/\tau_r} \frac{-\mathrm{Li}_2\left(-2\pi^2 N_0^{\max} R_{\mathrm{d-d}}^3 \mathrm{erf}(\sqrt{t/\tau_r})/3\right)}{2\pi^2 N_0^{\max} R_{\mathrm{d-d}}^3 \mathrm{erf}(\sqrt{t/\tau_r})/3}. \tag{4}$$

Here, $N_0^{\max} = I_0 \frac{\alpha\sigma}{\pi a^2}$ denotes the maximum STE concentration at $\rho = z = 0$. $\mathrm{Li}_2(x)$ is the dilogarithmic function defined as $\mathrm{Li}_2(x) = \int_0^x s^{-1} \ln(1-s) ds$, and $\mathrm{erf}(x)$ is the error function.

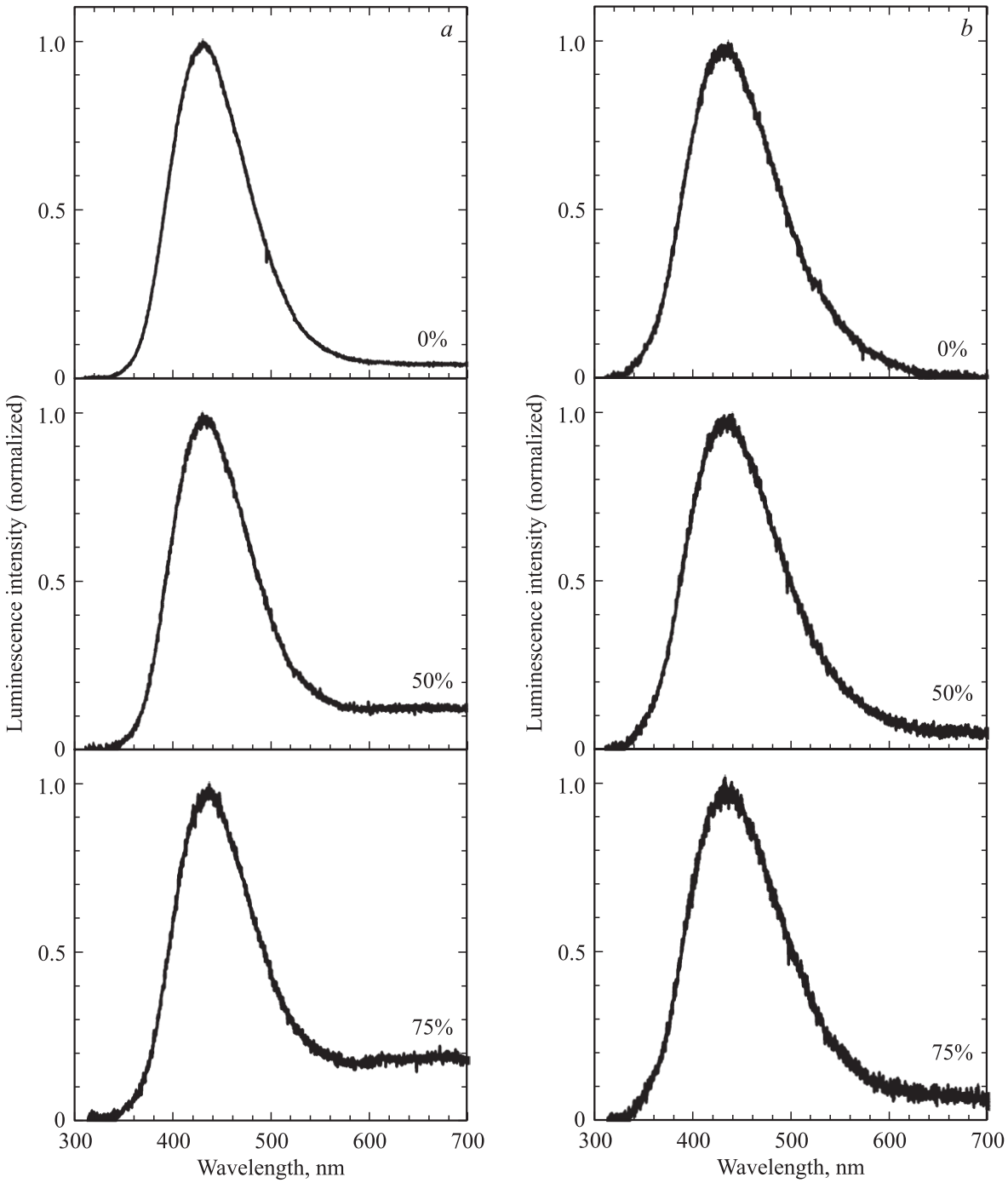

Figure 1. Luminescence spectra of a $CaWO_4$ crystal at 8 (*a*) and 300 K (*b*), excited with 89.84 eV photons for different attenuation levels (0, 50, and 75%) of the FEL beam.

Using Eq. (4), model curves were fitted to the data sets of the decays curves at 8 and 300 K shown in Fig. 2. For this procedure, values of $\alpha = 10^5\,\mathrm{cm}^{-1}$ and $a = 75\,\mu\mathrm{m}$ were used. The fitting was performed for a set of 9 decay curves at 8 K sample temperature, and a set of 10 curves for 300 K. In this routine, the parameters $R_{\mathrm{d-d}}$ and τ_r were fitted using the full data sets, and the number of photons I_0 was optimized for each individual decay curve. The value of σ was disregarded, as it always appears as a factor to I_0 in Eq. (4), and no experimental data exist to give a good extimate for its value. From point of energy conversation, the number of electron-hole pairs that can be created is $n_{e-h} = E_{\mathrm{ph}}/\beta E_g$ (E_{ph}: energy of incident photon, E_g: energy gap, β: conversion efficiency, typical values are 2–3), as discussed in [11]. Taking into account the values ~ 7.0 and 4.7 eV required for creation of free electron-hole pairs

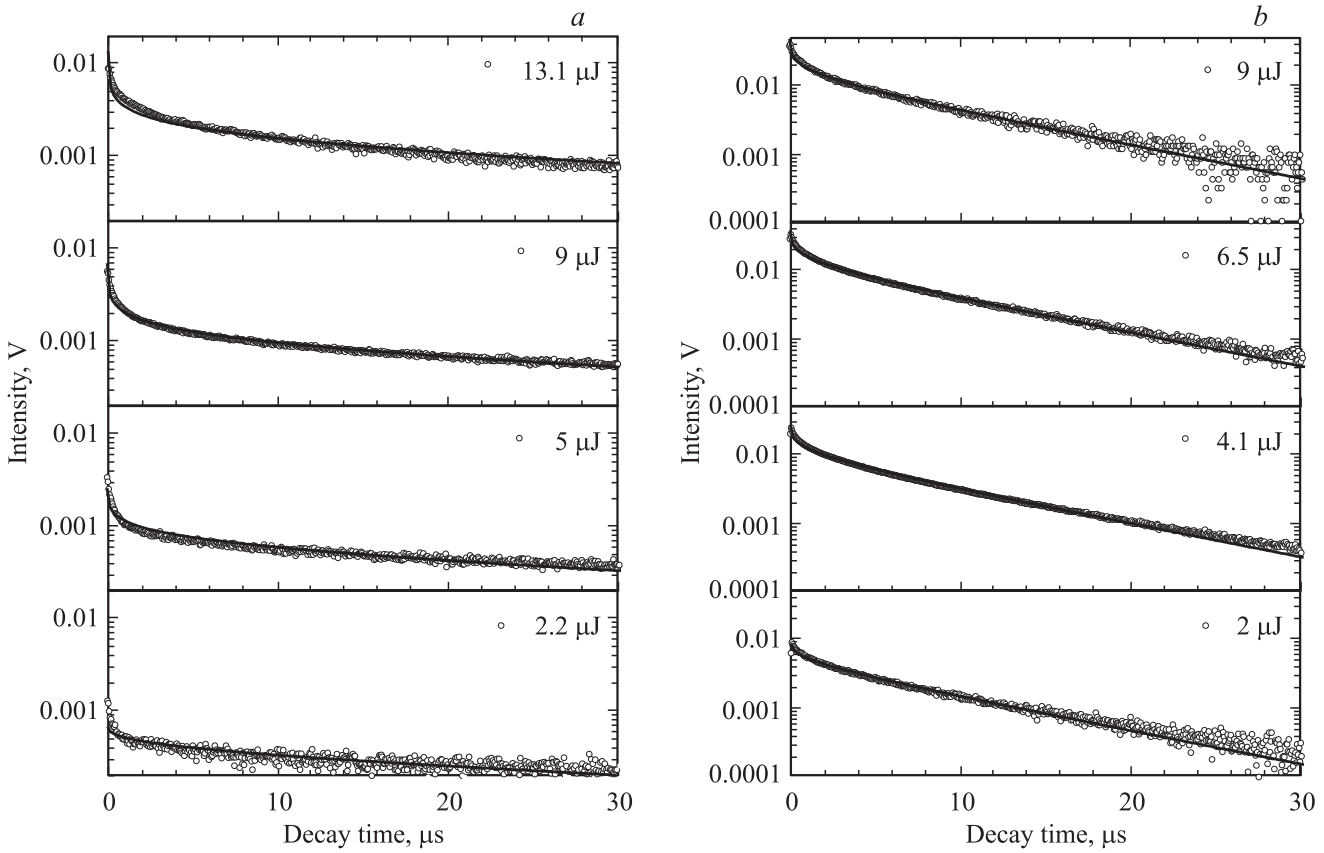

Figure 2. Measured (circles) and modeled (lines) decay curves for $CaWO_4$ at 8 (a) and 300 K (b) under excitation with 86.84 eV FEL pulses of different pulse energies.

and free excitons in $CaWO_4$ [12], the excitation by 89.84 eV photons could result in up to 19 unrelaxed excitons, but considering the formula above, the actual conversion is significantly less effective. Still, a σ of 6 is realistic for the given photon energy.

The resulting decay curves from the fitting procedure are given for four different FEL pulse energies at 8 and 300 K in Fig. 2. The shared parameters $R_{\text{d-d}}$ and τ_r were calculated as $R_{\text{d-d}} = 4.34$ nm (8 K) and 2.93 nm (300 K), as well as $\tau_r = 59.8\,\mu$s (8 K) and $9.1\,\mu$s (300 K). Decay times of $360\,\mu$s were reported in [13] for STE emission in $CaWO_4$ at 8 K under photoexcitation into the excitonic band. The obtained values for σI_0 are displayed in Fig. 3, b as a function of the pulse energy. For comparison, the peak values of the measured decay curves are shown in Fig. 3, a.

The overall agreement between the simulated and measured decays as shown in Fig. 2 is rather good, especially considering that the fit curves for each temperature only differ in the parameter σI_0 for the number of initial excitons. Comparison of this number with the measured maxima of the decay curves (Fig. 3) shows again good agreement regarding the general dependence on pulse energy. More problematic is the comparison between the results for the number of excitons I_0 and the number of photons $I_{0,\text{exp}}$ calculated from the experimental pulse energy (dotted line in Fig. 3, b). Considering our previously estimated value for σ of ~ 6, the fit values for I_0 lie about one order of magnitude lower than the measured ones. A comprehensive explanation for this discrepancy cannot be given at the moment, but several factors should be considered. First, the Gaussian distribution of the beam intensity might be incorrect for the FEL, and the values used for a and α are also extimates. In addition, the first initial nanoseconds of the decays are not resolved in the spectra, which might influence the accuracy of the calculations. Some influences not covered by the model should be taken into account as well. Notably, the possibility of triple correlations of excitations may play a role in the initial phase of the decay, and also the role of various non-radiative processes (e. g., trapping of $e-h$ pairs at impurities) is not considered at all.

The values for τ_r that were produced in the model agree well with the measured decay behavior at longer decay times as well as with literature data. It should be noted here that the decay times for the STE luminescence depend strongly on the temperature in the range below ~ 40 K [10]. The difference between the values for $R_{\text{d-d}}$ obtained for the two temperatures is probably still within the error margin that is to be expected for this fitting procedure, so that we should consider a single value $R_{\text{d-d}}$ between 3 and 4 nm.

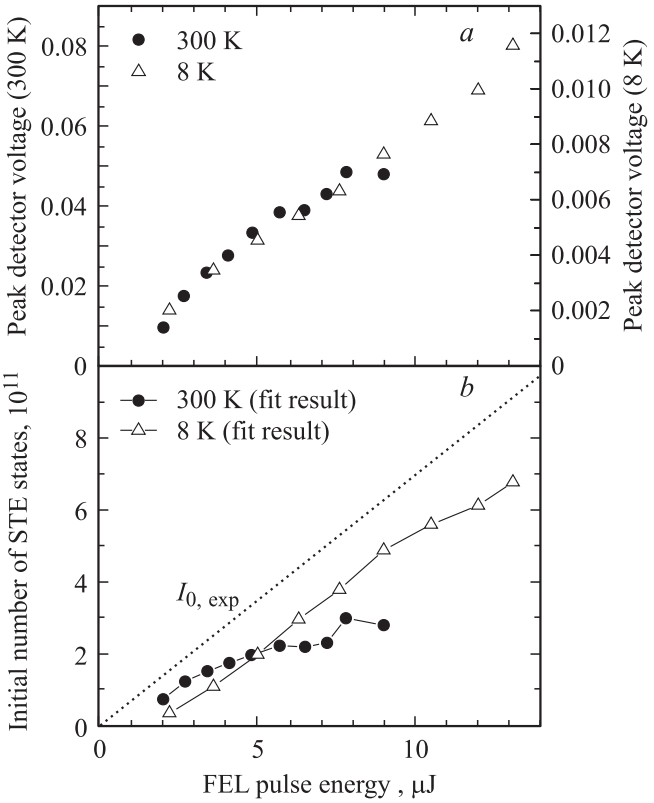

Figure 3. *a*) Measured peak values for the decay curves of $CaWO_4$ as a function of the FEL pulse energy, taken at temperatures 8 and 300 K. *b*) Calculated number of photons per pulse as fitted to the experimental decay curves for different pulse energies and sample temperatures 8 and 300 K. Dotted line: number of STEs for a quantum yield of 1 based on the number of photons per pulse calculated from the pulse energy ($I_{0,\mathrm{exp}}$).

This value corresponds well to the results obatined for $CdWO_4$ under high-order harmonic generation (HHG) laser excitation as reported in [9].

4. Conclusions

The investigation of $CaWO_4$ crystals under XUV FEL radiation with high intensity has given new insight to the exciton interaction under high STE concentrations. The non-exponential deviations in the decay curves could be satisfactorily reproduced within the framework of the excitonic self-quenching model. This process can also explain the non-linear luminescence yield that is observed for pulse energies $> 5\,\mu$J in Fig. 3. The analysis shows clearly that the photon densities achieved in the experiment lie above the threshold where excitations can be considered interaction free, and thus non-linear effects come into play when luminescence is considered. In the $CaWO_4$ sample, as well as in other crystals, no major changes in emission spectra were found that could indicate rediation damage, but in visual inspection of the samples after the irradiation, pitting of the crystal surfaces due to the FEL was observed on a macroscopic scale. Hopefully, measurements with a more collimated beam with a reduced spot size are possible in the future to test our model under more extreme conditions. Aside from FEL based research, excitation with powerful HHG has provided us with complementary data for $CdWO_4$ [9,14].

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