Exciton-exciton interactions in $CdWO_4$ irradiated by intense femtosecond vacuum ultraviolet pulses

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Exciton-exciton interaction is experimentally revealed and quantitatively analyzed in a wide band-gap scintillator material $CdWO_4$. Under high-intensity femtosecond vacuum ultraviolet excitation, the $CdWO_4$ luminescence is quenched, while its decay becomes essentially nonexponential. We propose an analytical model, which successfully reproduces the decay kinetics recorded in a wide range of excitation densities. The dipole-dipole interaction between excitons leading to their nonradiative decay is shown to be the main cause of a nonproportional response common for many scintillators.

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The interaction of electronic excitations is widely studied for semiconductors in the form of bulk crystals, quantum wells, or quantum dots. Exciton-exciton interaction is less investigated in insulators, where the excitonic radius is much smaller (Frenkel excitons) and very high-excitation density must be achieved to reveal the phenomenon. Recently, however, new sources, free electron, and plasma x-ray lasers, or those based on high-order harmonics generation, have extended the availability of ultrashort and intense light pulses into the vacuum ultraviolet (VUV) domain. This allows creation of high-density electronic excitations in wide band-gap dielectrics within a time range shorter than most of the relaxation processes. The spatial and temporal beam properties offer the possibility of studying densely excited matter under extreme but well-controlled experimental conditions.

It has been commonly accepted that the interaction of electronic excitations is a key factor responsible for nonproportional response of scintillators, one of the most important limitations in scintillator operation (see, e.g., Refs. 1 and 2). So far, high-energy photon and particle beams have been applied in the studies of the relevant phenomena, which prohibited the detailed understanding of the underlying mechanisms due to the diversity of the relaxation processes involved.[2]

In this Brief Report, we present the results of the experimental and theoretical studies of the elementary processes of the interaction of Frenkel excitons created in a $CdWO_4$ scintillator using short and intense VUV pulses provided by the generation of high-order harmonics of a titanium-sapphire laser in a rare gas. The method for the determination of microscopic interaction parameters of self-trapped excitons (STEs) in wide-gap materials is proposed for nonhomogeneous excitation conditions. The luminescence decay kinetics is shown to be a direct and sensitive probe of exciton-exciton interactions under high-density excitation.

$CdWO_4$ is widely used as a scintillating material in computed tomography and industrial testing due to its radiation hardness and intense intrinsic luminescence at 300 K.[3] The luminescence centered at 500 nm is due to the radiative decay of Frenkel-type self-trapped molecular excitons localized at oxyanion complexes.[4] The main decay component of the triplet STE is 15 μs at room temperature,[5] but under different irradiation conditions also much shorter decay components, 1.1,[6] 2,[7] and 5 μs,[8] have been reported. The differences observed in the decay kinetics could imply different densities of electronic excitations created by x ray or γ quanta of different energies used in the studies of scintillation response. Thus, small STE radius, long decay time, experimental hints about probable excitation density effects motivated us to choose $CdWO_4$ for the present study.

The experiments were performed at the Saclay laser facility PLFA. The setup allows generating VUV pulses and fo-

cusing them onto the sample at intensities up to 2×10^{10} W/cm^2, which induces a peak electron-hole pair density $N_0^{\max}$ as high as 2.5×10^{20} cm^{-3}. An amplified titanium-sapphire laser system delivers 35 fs pulses at 800 nm with pulse energy of up to 12 mJ at 1 kHz repetition rate. In the first vacuum chamber, the beam is focused into a gas cell with Xe flow at a pressure of 3–4 mbar. The nonlinear interaction of intense infrared beam with Xe atoms leads to the generation of coherent VUV light, which consists of the odd harmonics of the fundamental, extending up to orders 21–23. From 35 fs laser pulse the expected VUV pulse duration is 10–15 fs.[9] In the next two chambers, the collinear VUV and remaining infrared beams are separated using silica plates and a 100-nm-thick Al foil, and the VUV beam is focused onto the sample with a platinum mirror. The VUV light is mainly composed of the four harmonics 15–21, i.e., photons with energies from 23 to 32 eV. The number of VUV photons per pulse is estimated to be 5×10^7 in agreement with the expected conversion efficiency of 10^{-5}.[10] The incident photon flux is varied within 2 orders of magnitude by moving the sample along the beam axis and thus changing the spot size instead of the number of VUV photons per pulse. Luminescence spectra are recorded with a charge-coupled device (CCD) camera. The decay kinetics at a selected wavelength is studied with a fast photomultiplier using the time-correlated single photon counting technique with a 100 ps resolution.

The experimental results clearly show the dependence of luminescence properties of $CdWO_4$ on excitation density (Fig. 1). The decay curves increasingly deviate from the exponential law at higher intensities. The decay is much faster at the initial stages, and then gradually slows down approaching exponential decay with a typical time of 15 μs observed under optical excitation.[5] Along with the higher decay rate, a decrease in the total STE emission is observed at higher excitation densities (inset of Fig. 1), whereas the spectral shape of the emission band remains unchanged. The decrease in the steady-state luminescence is well correlated with the integrals of decay curves taken over the first 60 μs [Fig. 3(b)]. These data indicate the existence of a nonradiative recombination process with an efficiency depending on the excitation density, which competes with the luminescence.

To perform a quantitative analysis of the dependences of the luminescence yield and decay kinetics on excitation density, we propose the following hypothesis. The relaxation of VUV-induced electronic excitations ends rapidly with formation of self-trapped excitons in $CdWO_4$. If the density of STEs is high enough, the dipole-dipole interaction leads to a kind of the Auger process, $\mathrm{STE}+\mathrm{STE}\rightarrow\mathrm{STE}^*$. In other words one STE decays emitting a longitudinal virtual photon, whereas after its absorption the second one is excited and subsequently ionized, creating an electron-hole pair. The rate of such process can be written in terms of the theory of dipole-dipole energy transfer,

$$w_{d-d}(R)=\frac{1}{\tau_r}\left(\frac{R_{d-d}}{R}\right)^6, \tag{1}$$

where τ_r is the STE radiative lifetime and R_{d-d} is the dipole-dipole transfer radius, which can be expressed in terms of

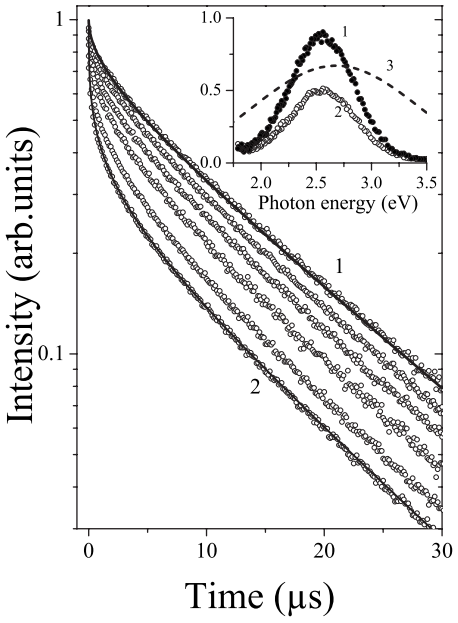

FIG. 1. Normalized decay curves of $CdWO_4$ emission, recorded at the same intensity but different densities of VUV excitation (circles). Curve (2) corresponds to the focal position with the highest excitation density (spot diameter 10 μm), curve (1) corresponds to 64 times lower density (spot diameter 80 μm). Solid lines show the best fit applying the proposed model. The inset represents the luminescence spectra recorded at the lowest (curve 1) and the highest excitation density (curve 2), and the transient absorption spectrum (curve 3) (Ref. 5).

emission and absorption line shapes.[11] The absorption and emission bands of the STE almost completely overlap in the case of $CdWO_4$ (Ref. 5) (inset of Fig. 1), thus maximizing the range of the dipole-dipole interaction.

Models describing the time evolution of emitting centers have been derived for the case of homogeneous excitation density and constant concentration of acceptors.[9] In our case, the donor and acceptor concentrations (both STEs) are time dependent and their initial distribution is inhomogeneous. This gives rise to complex decay kinetics, and a more general formalism has to be developed. The evolution of STEs concentration $n(\mathbf{r},t)$ must take into account their annihilation due to Förster dipole-dipole interaction (see, e.g., Refs. 11–13). In the simplest form the equation for the concentration is

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

where the bimolecular rate of reaction $\gamma(t,\mathbf{r})$ is time dependent. If the initial distribution is noncorrelated, and the exciton diffusion is negligible; this bimolecular rate is inversely proportional to the square root of time,

$$\gamma(t,\mathbf{r})\equiv\gamma(t)=(2\pi^{3/2}/3)R_{d-d}^3(t\tau_r)^{-1/2}, \tag{3}$$

but does not depend on initial concentration, thus eliminating dependence on $\mathbf{r}$. This approximation is valid for R_{d-d} larger than both the exciton radius and the diffusion length over

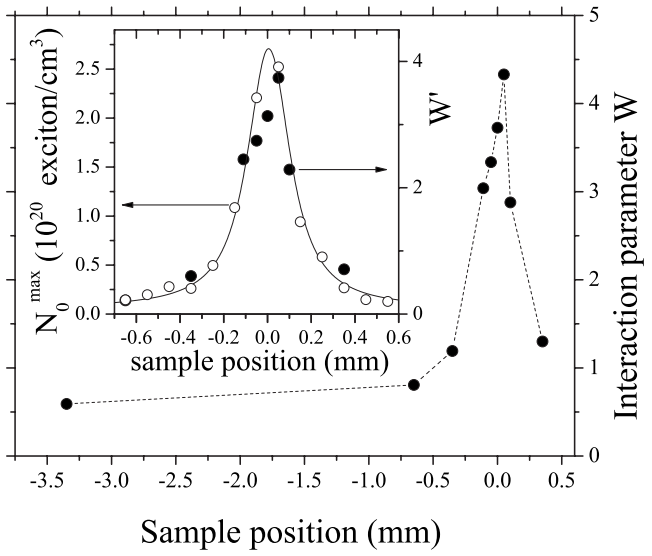

FIG. 2. Values of the interaction parameter W (filled circles) obtained from the fitting of the experimental decay curves using Eq. (4). Inset: density of excitons $N_0^{\max}$ in the spot center (open circles), Lorentz fitting of this density (solid curve), and corrected interaction parameter W' (filled circles).

time τ_r, and for low initial concentration (no more than two STEs in a sphere of radius R_{d-d}).

Equation (2) can be easily solved,

$$n(\mathbf{r},t) = n(\mathbf{r},0)e^{-t/\tau_r}\left[1 + \frac{2\pi^2}{3}n(\mathbf{r},0)R_{d-d}^3\,\mathrm{erf}\left(\sqrt{\frac{t}{\tau_r}}\right)\right]^{-1}, \tag{4}$$

where $\mathrm{erf}(x)$ is the error function. For the laser beam with Gaussian intensity distribution over its cross section, the initial concentration of excitations is $n(\rho,z,0) = I_0(\alpha\sigma/\pi a^2)e^{-\rho^2/a^2-\alpha z}$, where a is the radius of light spot on the crystal surface, $\boldsymbol{\rho}$ is the two-dimensional coordinate in the surface plane, the z axis is directed into the crystal, α is the absorption coefficient, I_0 is the total number of photons per pulse, and σ is the mean number of STEs produced by a VUV photon. From the excitation spectra[14] σ can be estimated as 2–3 for photons in the range from 23 to 31 eV. The peak density of STEs equals to $N_0^{\max} = I_0(\alpha\sigma/\pi a^2)$. To obtain the emission intensity one has to integrate Eq. (4) over the spatial coordinate $\mathbf{r} = \{\boldsymbol{\rho}, z\}$, resulting in

$$I_{\mathrm{lum}}(t) = \frac{\sigma I_0}{\tau_r}e^{-t/\tau_r}\frac{-\mathrm{Li}_2[-2\pi^2 N_0^{\max}R_{d-d}^3\,\mathrm{erf}(\sqrt{t/\tau_r})/3]}{2\pi^2 N_0^{\max}R_{d-d}^3\,\mathrm{erf}(\sqrt{t/\tau_r})/3}, \tag{5}$$

where $\mathrm{Li}_2(x) \equiv \Sigma_{k=1}^{\infty} z^k/k^2$ is the dilogarithmic function. Thus, the shape of the decay curve depends only on the dimensionless interaction parameter $W = N_0^{\max}R_{d-d}^3$, which is proportional to the number of excitons at the spot center within the sphere of the dipole-dipole transfer radius. For small argument of the dilogarithmic function the last fraction in Eq. (4) equals to $1-(\pi^2/6)N_0^{\max}R_{d-d}^3\,\mathrm{erf}(\sqrt{t/\tau_r})$ and shows a square root decay behavior at the initial stage ($t \ll \tau_r$). At longer times ($t \gg \tau_r$) the decay becomes single exponential with the radiative decay time τ_r. The decay curves calculated using

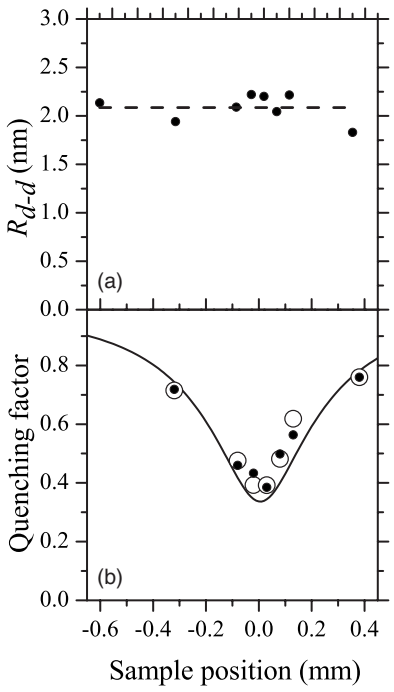

FIG. 3. (a) The dipole-dipole energy transfer radius R_{d-d} calculated from measurement of exciton density and corrected interaction parameter W' presented in Fig. 2. (b) Luminescence quenching factor versus position on the sample relative to the focal point: the integral of the decay curves for the first 60 μs (filled circles) and the total yield of luminescence, calculated by the integration of luminescence spectra (open circles). Solid line: deduced from the model [Eq. (4)] quenching factor $Q(W) \equiv (\sigma I_0)^{-1}\int_0^{\infty} I_{\mathrm{lum}}(t)dt$ calculated using the Lorentz fitting of the exciton density from the inset of Fig. 2.

formula (5) by adjusting the only fitting parameter W are drawn in Fig. 1 for the highest and lowest excitation densities. The corresponding W values are shown in Fig. 2. One can see that even at low-excitation densities, the interaction parameter is nonzero. Indeed the decay curves measured even far from the smallest focal spot still display a nonexponential behavior at short times. This effect is assigned to the impact ionization (see, e.g., Ref. 15), where primary electrons relax rapidly due to the inelastic scattering, producing the primary and secondary electron-hole pairs, and finally excitons, at the distances smaller or comparable to R_{d-d}. The fraction of the interaction parameter induced by the impact interaction is constant at a fixed photon energy and estimates to $W_0 = 0.6$ in our conditions. The corrected values $W' = W - W_0$ are shown in the inset of Fig. 2. From this, since the maximum density at the center of spot $N_0^{\max}$ is determined from our measurement of pulse energy and size, we calculate the parameter R_{d-d} [Fig. 3(a)]. The values of R_{d-d} found from the fitting of the decay curves remain constant over the whole range of excitation densities applied, giving us confidence concerning the hypothesis of a competition between radiative recombination and dipole-dipole interaction underlying the present model. The mean value of dipole-dipole interaction parameter 2.10 ± 0.15 nm corresponds to the separation of interacting excitons roughly by four lattice constants [$a = 5.029$ Å, $b = 5.859$ Å, and $c = 5.074$ Å (Ref. 16)].

Beside Förster interaction characteristics, the diffusion parameters have also been estimated from the deviation of excitonic emission decay from the exponential law in wide-gap semiconductors (see, e.g., Ref. 17). In the case of $CdWO_4$, however, the intensity of the emission of small radius Frenkel excitons remains practically constant up to room temperature, where its stability is estimated to be $-0.3\%\,^{\circ}C$.[7] For that reason in first approximation, one can neglect the effect of exciton diffusion on exciton-exciton annihilation in this crystal. High-excitation densities may also result in the formation of trions and other multiexciton complexes, which are possible but uncommon in wide-gap crystals.[18] The contribution of charged Frenkel excitons (trions) in exciton-exciton annihilation can be obviously disregarded due to the Coulomb repulsion of charged excitations.[19]

To conclude, we have shown that a dramatic modification of the luminescence emitted by a $CdWO_4$ scintillator occurs both in decay shape and intensity when high-excitation densities are reached. The observed changes are interpreted as a result of competition of the STE radiative decay with their nonradiative recombination due to the dipole-dipole interaction. Exiton-exciton interaction explains the appearance of short decay components in $CdWO_4$ exposed to various kinds of ionizing radiation. Such a modification of decay kinetics due to bimolecular interactions has already been reported for semiconductors.[20–22] However, exciton-exciton interaction is so far a nontrivial phenomenon in tungstates, considering the small radius of the Frenkel excitons, and consequently extremely high-excitation densities necessary. To our knowledge, such a process have never been analyzed earlier in wide-gap materials, although experimental indications to the possibility of an Auger-like process in STE recombination has been mentioned for $PbWO_4$ and $ZnWO_4$ crystals.[23,24] A similar behavior is observed in other scintillators as well ($CaWO_4$ and BaF_2), implying a more general character of the above-described phenomenon. The coherence of the proposed model with experimental data confirms the leading role of the dipole-dipole interaction in exciton annihilation responsible for the nonproportional response of scintillators. The quantitative handling of another important issue, the impact ionization, becomes possible on the basis of the present study. Valuable information about the efficiency of impact ionization, its energy dependence, or the average distance between primary and secondary electrons can be obtained by monitoring the decay time of the luminescence under different excitation conditions. Derived from general principles the proposed theoretical model is applicable in the analysis of time-dependent relaxation phenomena in various wide-gap materials exposed to nonhomogeneous high-energy and/or high-density radiation.

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