

Femtosecond laser pulse excitation of electrons and excitons in CaF_2 and SrF_2

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Abstract

Conduction band electrons, valence holes and subsequently self-trapped excitons (STEs) are created in CaF_2 and SrF_2 by two-photon absorption of 5.9 eV photons. Transient absorption after femtosecond pulse excitation is measured at probe wavelengths of 3.0 eV and 4.4 eV, respectively. Transient absorption of 3.0 eV photons yields a fast initial response in SrF_2 due to absorption by conduction band electrons, while in CaF_2 we sample the F centre part of the STE at 3.0 eV and determine its formation time constant to be 690 fs. Excitation at 3.0 eV also yields a reduction in STE luminescence sampled nanoseconds after STE creation that is attributed to a forced recombination of the nearest-neighbour defect pair. Probing with 4.4 eV photons yields much weaker absorption but confirms results for 3.0 eV photons. Additionally we observe stronger absorption due to the formation of long living defects.

1. Introduction

Calcium difluoride is an important material for optical applications in the ultraviolet spectral region [1] because of its wide band gap of about 12 eV and its convenient optical and mechanical properties. Highest quality single crystals are very transparent in the visible and ultraviolet spectral regions, but residual absorption, mostly related to linear absorption due to defects produced by surface preparation can result in a degradation of optical quality and leads to damage in high power applications [2]. For photon energies above 5 eV and irradiation with ultrashort laser pulses, however, there is the additional problem of creation of intrinsic defects due to multi-photon absorption of ultraviolet photons. For the further application of CaF_2 optical components for the ultraviolet spectral region, it is important to clarify in detail the absorption mechanisms, the dynamics of intrinsic transient defect formation and the question of to what extent transient defects are converted into long living species leading to incubation and permanent degradation. In the present contribution we address the first two questions.

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Although intrinsic defect formation in alkali halides caused by ultrafast laser radiation has been extensively treated [3], only a few picosecond time-resolved experimental results are available on defect formation in alkaline-earth halides [4]. This is mainly due to the fact that creating intrinsic defects with ultraviolet pulses in these wide-gap materials requires intense ultraviolet pulses of photons which have only recently become available. The processes of defect formation are basically the same for alkali and alkaline-earth halides but they differ in detail related to differences in crystalline structure. The primary process is an excitation of conduction electrons and valence holes or directly a free exciton that rapidly localizes into a self-trapped exciton (STE). As shown first by Hayes and colleagues [5, 6] the STE in alkaline-earth fluorides consists of a molecular ion similar to an H centre (hole on interstitial fluorine) and an F-centre-like part (electron in fluorine vacancy). We excite STEs by two 5.90 eV photons crossing the band gap, and probe defect formation by measuring the transient absorption in bands corresponding to the H and F centre parts of the STE. In CaF_2 we probe these bands with 4.43 eV and 2.95 eV photons, respectively. For comparison, we repeat the experiments with SrF_2 having a smaller band gap energy than CaF_2 . We find marked differences in transient response which we attribute to conduction band electron states populated in SrF_2 that are not accessible by the same excitation energy in CaF_2 .

2. Experimental set-up

Femtosecond laser pulses were generated by a Ti:sapphire laser and used as seed pulses for a regenerative amplifier optically pumped by a Nd:YAG laser operating with a pulse repetition rate of 10 Hz. This system provided fundamental pulses (Fu) at a photon energy of 1.48 eV. We used beta-barium borate (BBO) crystals for frequency conversion providing pulses of the second harmonic (SH) at 2.95 eV, the third harmonic (TH) at 4.43 eV and the fourth harmonic (FH) at 5.90 eV. A synopsis with information about the main pulse parameters for the fundamental and all harmonic pulses is provided in table 1.

The experimental set-up used for measurements of transient absorption is schematically depicted in figure 1. The FH beam was directed to the sample by a dichroic mirror and focused onto the sample surface by a quartz lens with 25 or 30 mm focal length. By positioning the focal spot slightly in front of the surface, care was taken to avoid excessive intensity resulting in sample damage. The excitation pulse energy was monitored with a pyrometer detector and used to normalize the probe signal. By a set of dichroic and partially reflecting mirrors, the beams of SH and TH radiation were directed collinearly to the sample. However, the position of their foci differed slightly from that of the FH beam due to the chromatic error of the focusing lens. This is important for overlapping the beams inside the crystal. The FH beam illuminates a larger volume of the crystal than the beams with the other photon energies. The time delays between the pumping FH pulse and the probing SH and TH pulses could be independently varied by two delay lines inserted into the optical paths of the respective beams. For measuring transient absorption, a fraction of the incident and transmitted pulse energies was recorded by

Table 1. Parameters of laser pulses used in the experiments described in this paper.

Harmonics	Photon energy (eV)	Wavelength (nm)	Pulse length (fs)	Max. pulse energy
Fu	1.48	840	120	2 mJ/pulse
SH	2.95	420	< 230	25 μJ /pulse
TH	4.43	280	< 230	1 μJ /pulse
FH	5.90	210	< 270	12 μJ /pulse

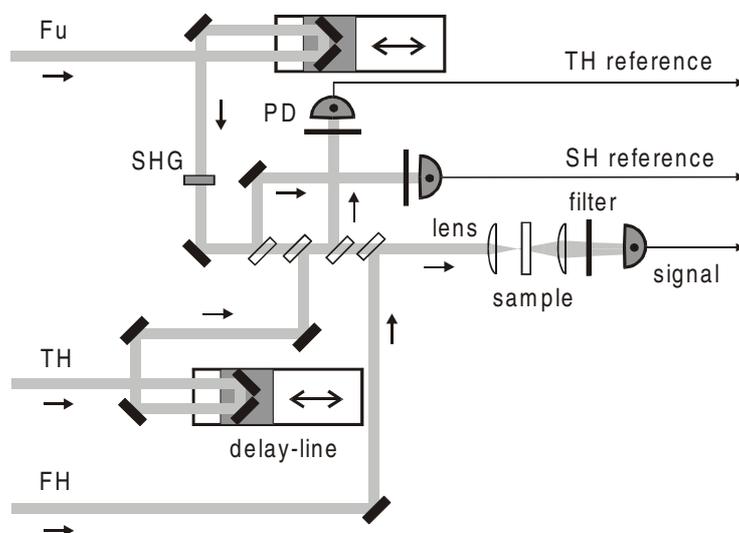


Figure 1. Experimental set-up for pump-probe measurements. The fourth harmonic beam (FH) is used as the pump pulse. The second harmonic beam (SH) and the third harmonic beam (TH) are used as probe pulses and can be independently delayed. Pump and probe beams are generated from the fundamental beam (Fu) by frequency conversion in non-linear crystals.

photodiodes (PDs) with a rise time of 10 ns. By placing appropriate optical filters in front of the photodiodes, we ensured that absorption measurements were neither influenced by pump light nor by non-linearities of the photodiodes. In the case of measurements with TH probe pulses, a prism was additionally used to separate the beams. The signals of incident and transmitted pulses were processed by two box car integrators sampling intensity only during the photodiode signal with single shot data storage. To improve the signal-to-noise ratio each value of one pump-probe delay was measured several times (typically 25 times). Data analysis was performed in the following way. For each delay time only these measured points were used which did not deviate by more than 15% from the mean value. After this selection, the transmitted signal was divided by the incident intensity signal to obtain a normalized transmission value. All such values for a given delay time were averaged. In most of the graphs shown here, we display the normalized transmission as a function of the pump-probe delay time.

During some experiments we also recorded the luminescence emitted nanoseconds after the pump-probe cycle. This was accomplished by a gateable optical multi-channel analyser sampling STE luminescence spectra during a time interval of 350 ns starting 30 ns after the pump pulse. For a set of randomly chosen delay times, the spectrally integrated luminescence intensity was measured and averaged over 100 irradiations. The resulting data are also displayed as a function of pump-probe delay time and can directly be related to the transient absorption data. More details of our experimental system and procedure to measure luminescence can be found in [7].

3. Results

In a first set of experiments, we investigated the response of the STEs to 2.95 eV probe pulses. As a general observation we note that after starting irradiation of the crystal with pump laser

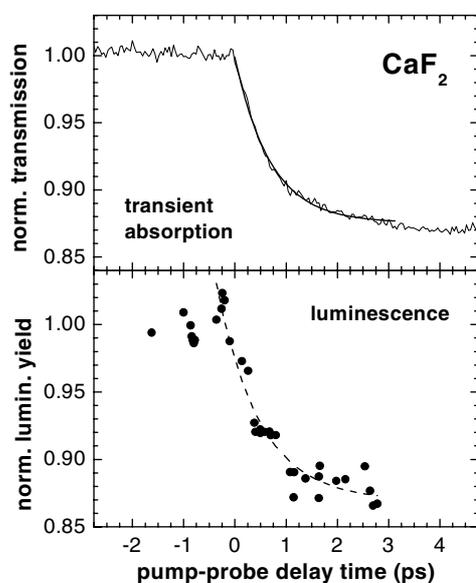


Figure 2. Dependence of the normalized transmission of 2.95 eV probe photons (upper frame) and the normalized STE luminescence yield (lower frame) on pump–probe delay in CaF_2 . Exponential functions are fitted to the data yielding time constants of 0.69 ± 0.01 ps and 0.84 ± 0.11 ps for absorption and luminescence measurement, respectively.

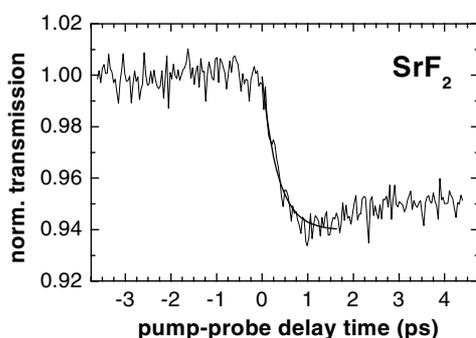


Figure 3. The normalized transmission of 2.95 eV probe photons as a function of pump–probe delay in SrF_2 . The exponential fit function establishes a time constant of 0.34 ± 0.03 ps.

light, we observed a reduction in probe light transmission independent of the pump–probe time delay that developed within minutes as quasi-exponential decay towards an equilibrium level. We attribute this to the formation of stable defects by the 5.90 eV photons that will be discussed in detail in a forthcoming paper. Here we note that the adjustment to an equilibrium level is a result of two competing processes, i.e. the creation of defects by 5.90 eV photon irradiation and their partial annealing by 2.95 eV photons. All measurements presented here have been performed under conditions where the variation due to the long-term decay was below the noise level.

Figures 2 (upper frame) and 3 show the respective transient absorption results for CaF_2 and SrF_2 . For both materials, a significant fraction of the probe beam light is absorbed within several picoseconds delay time in which the transmission drops to 0.87 of the original level

for CaF₂ but only to 0.95 for SrF₂. The transient behaviour differs remarkably for the two crystals. In the case of CaF₂ we observe a growth of the transient absorption signal that can well be fitted by a single exponential curve with a time constant of 0.69 ± 0.02 ps. SrF₂ shows a more complicated temporal behaviour. An initial steep growth of absorption is followed by a weak recovery before the signal levels off to a constant value. Fitting the first 1.63 ps after the excitation, we obtain a time constant of 0.34 ± 0.03 ps for the fast growth. In case of CaF₂ we repeated the transient absorption measurement and simultaneously recorded the STE luminescence yield as shown in the lower frame of figure 2. The luminescence data are noisier, but we can clearly identify the same time constant in luminescence depletion as in transient absorption growth. The dashed curve is the best exponential fit yielding a decay time of 0.84 ± 0.11 ps that agrees with that for transient absorption within the experimental error.

Results are markedly different when probing STEs with 4.43 eV photons, as demonstrated by transient absorption data shown in figure 4. The main feature here is a monotonic decay of transmission due to build-up of permanent absorption from the multiple pulses needed to acquire the data. Transient effects can barely be discriminated from noise. In general we observe for this probing photon energy a decay in transmission independent of delay time that does level off much slower to an equilibrium than for 2.95 eV photons. Transient effects are found to be much weaker, which has mainly to be attributed to experimental reasons. The intensity of the TH probing beam is much smaller and the beam profile is less perfect compared to that of the SH beam resulting in a higher noise level at a reduced signal amplitude. However, as will be discussed in the next chapter, from the STE spectral properties we also expect a weaker absorption signal when probing at 4.43 eV as opposed to probing at 2.95 eV. Due to these peculiarities, it is not possible to deduce a time constant for the decay in transmission related to the pump-probe delay time from TH transient absorption data and as a main result from this section we note the accumulation of absorption when exciting STEs and simultaneously irradiating with 4.43 eV photons.

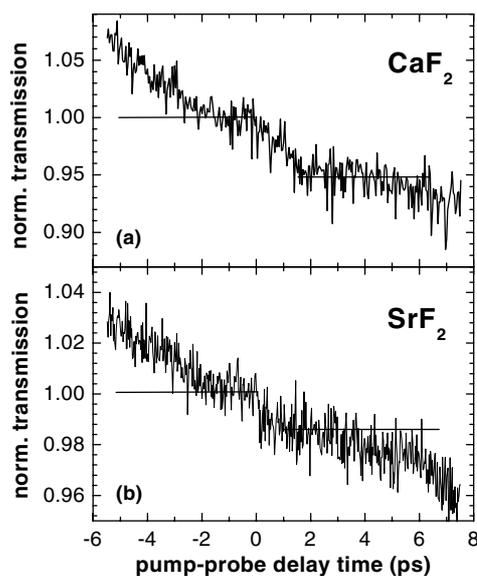


Figure 4. The normalized transmission of 4.43 eV photons versus pump-probe delay for CaF₂ and SrF₂, respectively.

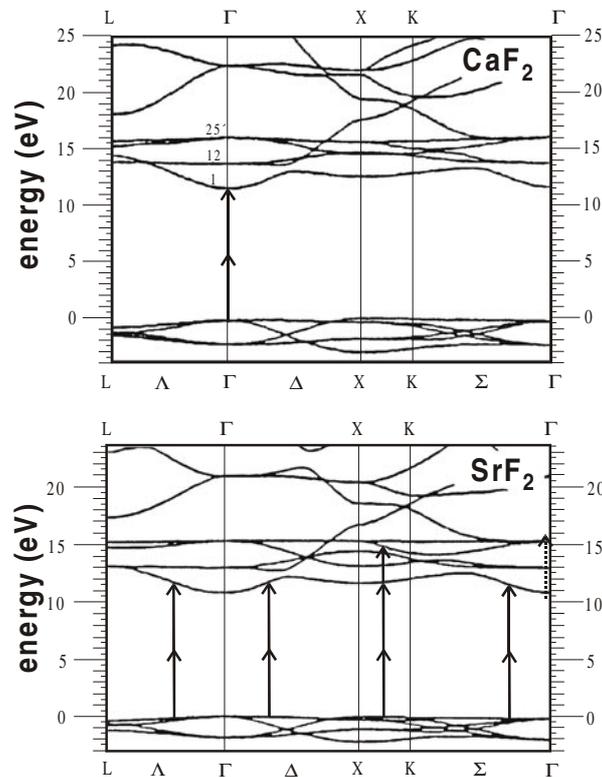


Figure 5. Calculated band structure of CaF_2 and SrF_2 from [8]. The band gaps were corrected according to experimental results of Rubloff [11] taking the minimum between the exciton peak and the conduction band. The arrows show possible excitations with photon energies used in this work.

4. Discussion and conclusion

Transient absorption following laser pulse excitation can be due to two different processes, namely absorption by STEs or by precursor states such as conduction band electrons or non-relaxed STE states. Depending on what process is effective, the observed decay times of the optical transmission have to be interpreted differently. We consider conduction band excitations of both investigated materials and illustrate possible optical transitions in schematic band structures [8] shown in figure 5. By two-photon excitation with 5.90 eV photon energy only the lowest minimum of the conduction band (1) is populated. While excitation is possible at various points of the Brillouin zone for SrF_2 , in the case of CaF_2 , energy conservation allows transitions only at the Γ point. In CaF_2 any further excitation by 2.95 eV photons or 4.43 eV photons is excluded by a missing match between the photon and transition energies at the Γ point and by selection rules because the transitions $\Gamma_1 \rightarrow \Gamma_{12}$ and $\Gamma_1 \rightarrow \Gamma_{25'}$ are forbidden [9]. For SrF_2 , however, transitions for 2.95 eV probing photons appear to be possible. Since band structures presented in figure 5 are based on calculations that have not been experimentally verified to our knowledge, there is some uncertainty regarding the exact energetic positions of the involved bands and possible transitions. Furthermore, it has to be kept in mind that the process of STE formation is accompanied by a considerable distortion of the lattice and

consequent local changes of the electronic band structure. However, qualitative conclusions drawn from band structure should remain valid and provide a straightforward interpretation for the different transient absorption behaviour of the two investigated materials. In CaF₂ the probe pulses can only excite STEs but not conduction band electrons and, therefore, the absorption transient in figure 2 reflects the dynamics of the STE formation. The fact that the absorption transient can well be fitted by a single exponential function for probing at a single photon energy indicates that the spectral absorption characteristics do not change dramatically during STE formation and, therefore, the observed time constant of 690 fs can be taken as a reliable value for the STE formation time in CaF₂.

To fully understand the interaction between SH and TH photons and STEs, we have to clarify which states are involved at the respective photon energies. To accomplish this, we recall that the STE absorption spectra of the investigated fluorides consist of two well separated spectral features where the lower energy peak is attributed to absorption by the F centre part of the STE while the higher energy peak is due to absorption by the H centre part [6]. For both materials, 2.95 eV photons from the SH beam interact with the F centre part while 4.43 eV photons from the TH beam are absorbed by the H centres, which offers the unique possibility of specifically addressing one or the other part of the STE. For SrF₂, however, the SH photon energy does not match well with the maximum of the absorption peak, which explains the weak transient absorption at 2.95 eV in this case.

For the explanation of the reduction in luminescence intensity related to transient absorption, we first note that an excitation from the STE or its precursor states into a delocalized state of the conduction band of the unperturbed lattice probably cannot occur with 3.0 eV photons, since consideration of the spectrum in analogy to F centres suggests that the photoionization threshold is above 5 eV [10]. Thus the apparent destruction of STEs in the lower frame of figure 2 should be due to a local recombination processes. We propose that the decrease of STEs is initiated by the excitation of the F centre part of the STE into the first excited state. This is a p-like state with a wavefunction extending much further than the s-like F centre ground state [10]. Therefore, there will be a larger overlap with the H centre part of the STE and, consequently, a higher probability for recombination. The luminescence of STEs recombining picoseconds after excitation is, however, not recorded by our detection system, where sampling starts 30 ns after excitation. Therefore, the forced recombination of STEs by SH radiation results in an effective suppression of the STE luminescence yield that is proportional to the number of STEs created in perfect accordance with experimental observation presented in the lower frame of figure 2.

The more complicated SH absorption transient observed for SrF₂ is interpreted in terms of a combined action of conduction band excitation and STE formation where the fast initial decay is attributed to absorption by conduction band electrons while STE absorption dominates the signal for larger delay times. The shallow minimum appearing at 1 ps is due to a turnover from one process to the other. This measurement, however, does not allow us to extract a time constant for the relaxation of conduction band electrons since the apparent decay time is close to the laser pulse duration and, therefore, dominated by the pulse structure rather than the electronic relaxation.

In conclusion of absorption results obtained for 2.95 eV photons we find that the observed transients are in agreement with the behaviour that would be expected from an analysis of the band structures of CaF₂ and SrF₂ in conjunction with the involved photon energies. The femtosecond spectral measurements of Thoma *et al* [4] in SrF₂ after 5.81 eV photon excitation should contain the conduction electron contribution. However, the observed spectrum even as early as 500 fs had as identifiable features only those of the known STE spectrum between 1.7 and 2.8 eV. Within the present suggestion that the earliest absorption is due to conduction

electrons, we must assume that such absorption is relatively featureless in the range of 1.7 to 2.8 eV [4].

As mentioned above, the absorption transients observed for irradiation with 4.43 eV photons cannot be well analysed due to experimental constraints, but results shown in figure 4 indicate that the involved time constants are similar to those observed for 2.95 eV irradiation. This is expected since switching probe beam light from SH to TH means probing the H centre part of the STE rather than the F centre part and, since these are two complementary defects annihilating each other upon recombination, all arguments from the discussion of SH results also apply to TH results. Additional processes of defect trapping or clustering are not relevant during the first picoseconds after excitation.

In summary, our experimental results allow us to draw some basic conclusions about ultra-fast spectroscopy of halides with the fluorite structure. Valence band electrons can be excited into the lowest conduction band via two-photon absorption of 5.9 eV photons. Further excitation of these conduction band electrons can be accomplished with photons of energy within a broad range determined by the conduction band structure; however, a precise determination of intra-band electron relaxation time would require pulses with a shorter duration than presently available. Electron excitation is followed by the formation of self-trapped excitons that can be probed by photons addressing the F or H centre parts of the STE. A prerequisite for the observation of the STE formation dynamics is that the probing wavelength is chosen in such a way that STE absorption is not superimposed by conduction band absorption. In our case this was accomplished for measurements on CaF₂ where we derived an STE formation time of 690 fs from transient absorption data. It was also shown that STE recombination can be forced by excitation of the F centre part of the STE and in all our experiments we found evidence for the formation of long living defects that will be the subject of a forthcoming paper.

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