Relaxation of electronic excitations in wide-gap crystals studied by femtosecond interferometry technique

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The method of time-resolved interferometry with the 100 fs temporal resolution was applied for the first time to study the relaxation processes of electronic excitations in complex oxides, tungstate crystals of $CdWO_4$ with the lattice of the wolframite type and $CaWO_4$ with the scheelite type lattice. Two stages of charge carrier relaxation, its very fast trapping in 200 fs resulting in self-trapped exciton formation and a relatively slow relaxation process in a picosecond time range probably due to the configurational relaxation within the oxyanion molecule and modification of the surrounding lattice, were revealed in tungstate crystals. The corresponding models of self-trapped exciton creation in tungstate crystals are discussed.

1. Introduction

The method of time-resolved interferometry has proved itself to be a powerful tool for study of the relaxation dynamics of free charge carriers and their trapping in solids. It has been sucessfully used to study the evolution of electronic excitation density in SiO_2, MgO and Al_2O_3 [1]. Measuring free electron lifetimes in the conduction bands of these systems allowed to distinguish the materials with and without self-trapping of excitons. Later the comparison of laser-induced carrier-trapping dynamics in SiO_2, NaCl and KBr was helpful in clarifying the machanisms of exciton self-trapping in these materials. An electron and a hole are simultaneously trapped creating an exciton in SiO_2, while trapping of holes is the initial stage of exciton formation in alkali halides [2]. In the present study, for the first time we have applied the method of time-resolved interferometry with the 100 fs temporal resolution to study the relaxation processes of electronic excitations in complex oxides, tungstate crystals of $CdWO_4$ with the lattice of wolframite type and $CaWO_4$ with the scheelite lattice. Both systems are characterized by a strong electron-phonon interaction; their emissions originate from self-trapped excitons localized at oxyanion sites [3,4]. The detailed machanisms of exciton self-trapping in these systems are not known. There are arguments in favour of a fast relaxation of an exciton due to a strong electron-phonon interaction in an oxyanion site as well as in favour of self-trapping of charge carriers before the exciton formation.

2. Experimental details

The samples studied were 2 mm thick optically polished $CaWO_4$ and $CdWO_4$ as well as 0.5 to 1 mm thick cleaved $CdWO_4$ plates of approximately 10×10 mm dimension.

The set-up for the time-resolved interferometry measurements has been described elsewhere [1,2]. The following experimental procedure was used in the present study. Two identical 790 nm probe pulses of 100 fs duration separated by 60 ps passed through a crystal and produced an interference pattern at the exit slit of the spectrometer. A high intensity pump pulse impinging the sample between the two probe pulses modified the electronic system of the sample and caused the change in the refraction index altering the interference pattern. This change was used to calculate the phase shift and absorption induced by the pump beam. Varying the delay between the pump and probe pulses the time dependences of the phase shift and absorption coefficient in the interval of 0–60 ps were recorded. We used for pumping 2nd, 3rd and 4th harmonics of a 790 nm Ti:Sapphire laser beam absorbed in the one-photon or multiphoton regime depending on the band-gap width of a crystal. All experiments were performed at room temperature.

3. Results and discussion

The band-gap width of $CaWO_4$ and $CdWO_4$ has been determined from the excitation spectra of recombination luminescence [5,6]. The threshold energy for free electron creation has been measured 5 eV in $CdWO_4$ and 7 eV in $CaWO_4$. Photoexcitation of the crystals at lower energies, approximately in the region of 3.7–5 eV in $CdWO_4$ and 4.7–7 eV in $CaWO_4$ at room temperature, produces mainly Frenkel molecular excitons localized at oxyanionic complexes WO_6 and WO_4, respectively. Thus, the excitonic band is relatively broad in tungstate crystals compared to simple oxides. The unique advantage of these materials in the time-resolved interferometry experiment is that using

different harmonics of a 790 nm fundamental laser beam along with multiphoton pumping at increased intensity we can in principle selectively create either excitonic or conduction band excitations in these crystals. The energies of the 2nd, 3rd and 4th harmonics of a 790 nm laser are 3.14, 4.71 and 6.28 eV, respectively. The energy 4.71 eV fits well for the excitonic absorption in $CdWO_4$, 3.14 eV lies in its transparency region, while 6.28 eV corresponds to the excitation of the electron-hole continuum. In $CaWO_4$, the value of 6.28 eV matches the region of the excitonic band, while the pumping with the 3rd harmonic produces mainly free charge carriers in a two-photon process $(2 \cdot 4.7 \, eV)$, but partly also excitons at a direct one-photon excitation fitting the very edge of the excitonic band. It should be mentioned that absorption coefficients within the excitonic absorption band are high (up to $10^6 \, cm^{-1}$) [7] and in the case of pumping by higher harmonics in the one-photon regime (4.71 eV for $CdWO_4$ and 6.28 eV for $CaWO_4$, respectively) the pumping pulse is absorbed in a thin surface layer of the order of 100 nm. On the other hand, pumping in the two-photon regime with the same resulting energy provides excitation of the electronic system in the crystal volume. The comparison of the time dependences of phase shifts in two pumping regimes provides additional information on relaxation dynamics of electronic excitations. The analysis of the temporal behaviour of phase is based on the model described in detail in [1,2].

Time dependences of phase shifts induced by injection of electrons into the conduction band of a crystal are shown for $CaWO_4$ and $CdWO_4$ in Figs 1–3. Fig. 1, b presents the space integrated phase shift as a function of time during the first 2.5 ps measured in $CaWO_4$ for pumping photon energy 6.28 eV from the excitonic region at the energy flux of 0.025 J/cm². No initial positive phase shift due to the Kerr effect at the moments of overlapping pump and probe beams is observed in such conditions, unlike the case of multiphoton pumping in a number of oxides and halides [1,2]. Several factors tend to reduce the Kerr effect in this case: 1) a short overlapping range of the pump and probe beams due to a high absorption coefficient in the excitonic region; 2) since the absorption is linear a weaker pump intensity was used, and probably the non-linear coefficient responsible for the Kerr effect was smaller. Then the phase shift value sharply changes to negative when electrons are injected near the bottom of the conduction band and thereafter to positive, reflecting the trapping processes. The trapping is very fast, its rate has been estimated to 200 ± 50 fs that obviously reflects the characteristic time of exciton formation. No dependence of the trapping rate on the intensity of pumping beam was observed. This might be indicative of a direct formation of excitons on the states of WO_4 molecular anion of $CaWO_4$, unlike the exciton trapping over the intermediate self-trapping of its hole component observed by the same method in NaCl [2]. At further relaxation stages, a slow decrease in the value of the positive phase shift is observed in time range of 1 to 20 ps (Fig. 1, c). The relaxation
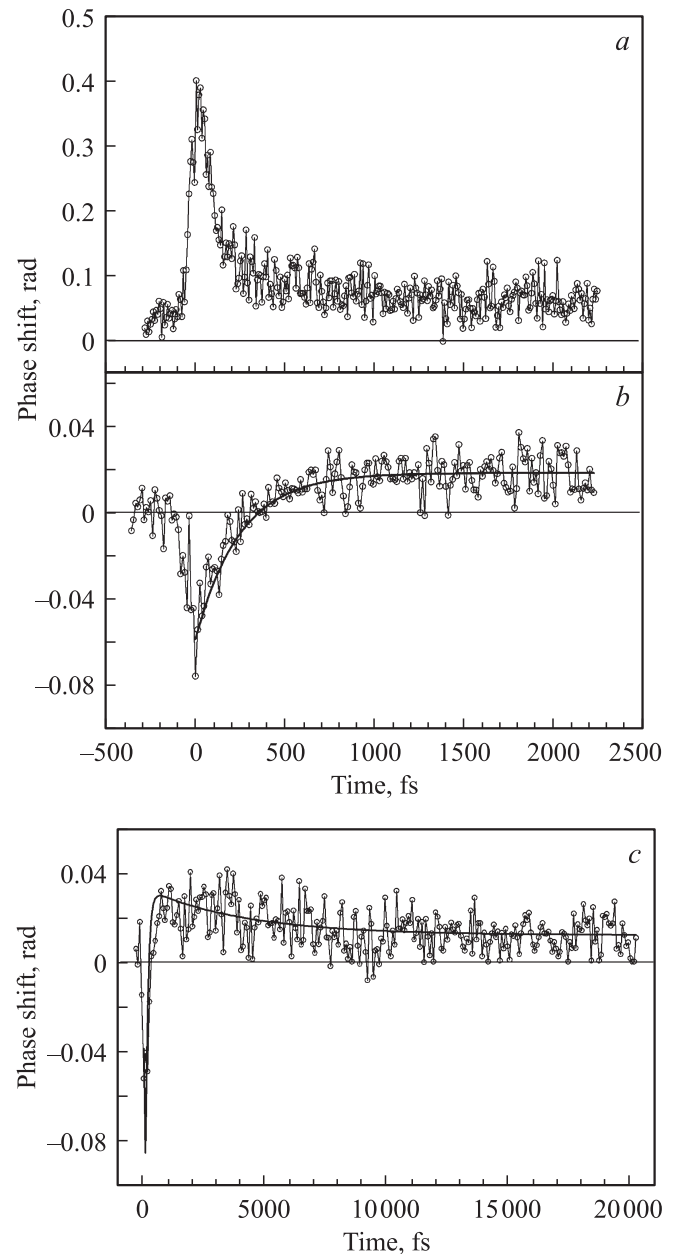

Figure 1. Time dependence of phase shift measured in a $CaWO_4$ sample for pumping by 4.71 (a) and 6.28 eV photons (b — short time scale, c — long time scale) at energy flux of 0.025 J/cm² at room temperature. Bold solid lines represent the best exponential fit with the time parameter 250 fs in (b) and two-exponential fit with the time parameters 160 fs and 5 ps in (c).

time in this region was estimated to 5.5 ± 2 ps. Such time scale is characteristics of relaxation processes involving the configurational changes in nuclear system [8,9].

At the pumping energies of 3.14 and 4.71 eV, when electronic system of the $CaWO_4$ crystal is excited in a multiphoton process, the negative phase shift due to the injection of free electrons into the conduction band is masked by the Kerr effect (Fig. 1, a). We could observe only the positive peak at the times of overlapping pump and
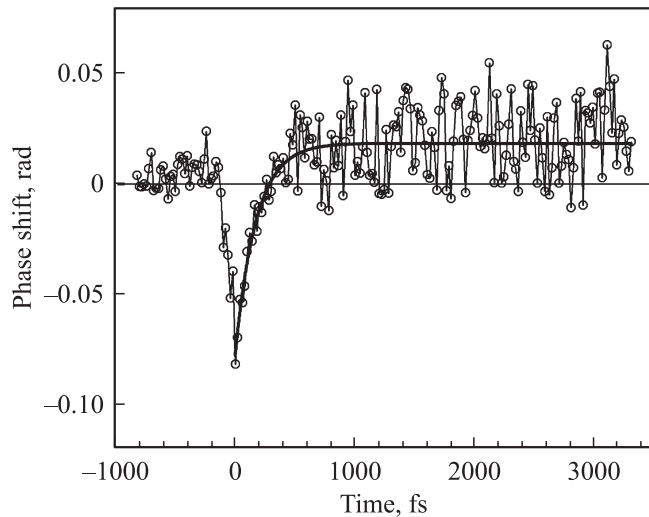
Figure 2. Time dependence of phase shift measured in a cleaved CdWO$_4$ sample for pumping by 6.28 eV photons at energy flux of 0.017 J/cm^2 at room temperature. Bold solid line represents the best exponential fit with the time parameter 170 fs.

probe beams and then immediately after that the decrease in the positive shift value due the relaxation within the trapping centre like in the case of the excitation by the 4th harmonic. The results are similar for both pumping energies and therefore shown only for 4.71 eV in Fig. 1.

The results obtained from CdWO$_4$ are to a certain extent sample dependent. Under the pumping by the 4th harmonic at 6.28 eV (at energy flux 0.017 J/cm^2) producing free charge carriers in a thin surface layer, both cleaved and polished samples demonstrated a very short electron trapping time (Fig. 3), equal to that observed in CaWO$_4$ (200 fs). It is obvious that hot electrons injected 1.3 eV above the electron mobility threshold reach the bottom of the conduction band very fast and in principle should form excitons ending in radiative or non-radiative decay. In the case of CdWO$_4$, however, we obtained somewhat different results for larger relaxation times in cleaved and polished samples. While in a cleaved sample the phase shift turns from negative to positive near in 400 fs and then gradually decreases to zero with the characteristic time of 6 ps (Fig. 3, *a*), that in a polished sample reaches zero value in about 1 ps and remains later unchanged (Fig. 3, *b*). The question whether such difference can be connected with different surface losses in these samples remains open now because of the lack of sufficient variety of experimental data. From general consideration the cleaved surface should be more substance specific, than the polished one, although the latter is more convenient for laser experiments. Generally, the absence of a phase shift at longer time delays could mean the absence of a trapping process or fast de-excitation due to non-radiative recombination of mobile electrons which reached the surface layer. However, a very bright luminescence observed in the experiment and a non-zero absorption measured along with the phase shift undoubtedly

confirm an efficient creation of self-trapped excitons in this process. A short interaction length of the probing beam with the excitations produced by the pumping beam in a surface layer could explain the very small phase shift observed, however, the phase shift can be reliably measured in the same conditions in CaWO$_4$. For that reason we find more probable the next explanation. It has been shown in [1], that the phase shift observed at large time delays should be positive, if the trapping occurs deep in the band gap, and negative, if the trapping takes place at the levels
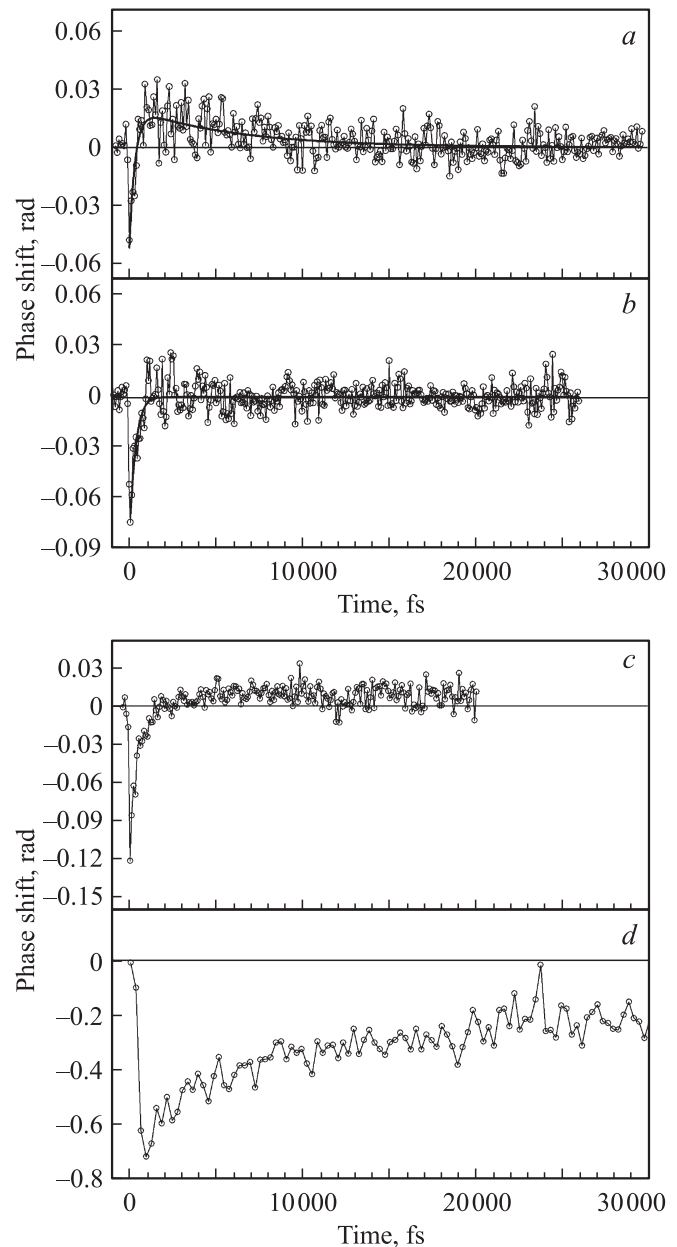

Figure 3. Time dependence of phase shift measured in cleaved (*a*) and polished (*b–d*) CdWO$_4$ samples for pumping by 6.28 (*a*, *b*), 4.71 (*c*) and 3.14 eV (*d*) photons at energy flux 0.017, 0.015 and 0.04 J/cm^2, respectively, at room temperature. Bold solid line in (*a*) represents the best two-exponential fit with the time parameters 250 fs and 6 ps.

localized at distance from the bottom of the conduction band smaller than the probe photon energy (1.56 eV in the present study). The near zero phase shift measured at large delays in $CdWO_4$ accompanied by the measurable absorption of the probe beam may indicate that the trapping level is located at nearly resonant distance of 1.5 eV from the bottom of the conduction band. This assumption seems plausible also from the energy point of view considering the band gap value of 5 eV [5] and emission band position at 2.5 eV [3] in $CdWO_4$, that leaves approximately 1 eV for the lattice relaxation after the exciton decay.

There is no difference in the temporary behaviour of the phase shift between cleaved and polished samples at pumping by the 3rd and 2nd harmonic (0.015 J/cm^2 and 0.04 J/cm^2, respectively). The energy of the 3rd harmonic 4.71 eV fits well for the excitonic region of $CdWO_4$, characterized by large absorpion coefficients, and correspondingly a thin layer is excited in this case as well. However, the phase shift arrives at small but reliable measurable positive values in both samples, clearly demonstrating exciton trapping processes at direct optical creation of the excitons. This experimental fact may be also indicative of a low mobility of self-trapped excitions in $CdWO_4$. It has been shown also for other oxides that surface losses increase when excitation energies exceed those necessary for exciton creation and reach the range where free charge carriers are created in the crystal (see, e.g., [10]).

At pumping by the 2nd harmonic (3.14 eV, 0.04 J/cm^2), which in the two-photon regime should fit for the electron-hole continuum in the crystal bulk, the phase shift remains negative during the whole measurement time, although the slow relaxation process is observed as well. Such a long lasting negative shift leads to the suggestion that the corresponding trapping level is localized at a distance from the bottom of the conduction band smaller than the probe photon energy (< 1.56 eV). Although we did not observe measurable absorption bands in the region around 3 eV, we cannot completely exclude the presence of defect-related states affecting the measurement results at high-intensity pumping by the 2nd harmonic. To reveal the states, which are populated under such conditions, additional investigations are necessary, including in particular the measurement of the phase shift dependence on the excitation intensity and time-resolved interferometry study at low temperatures.

4. Conclusions

Summarizing the experimental data obtained, one can conclude that the time for electron trapping and formation of Frenkel excitons is very short, equal to 200 fs in both $CaWO_4$ and $CdWO_4$. Such short electron trapping times are characteristics of the systems with strong electron-phonon interaction [1,2,11]. This result is in good agreement with general knowledge about tungstate crystals, in which self-trapping of excitons has been proven for a large number of materials, but also self-trapping of holes [12,13] and electrons [14] has been shown. The independence of

the electron trapping rate on the pumping intensity could indicate a direct creation of self-trapped excitons without intermediate self-trapping of holes. To prove this suggestion, however, more extended investigations are necessary. At least for $CaWO_4$ it is in contradiction with the model of recombination formation of excitons suggested in [10]. The stabilization of the phase shift at positive values in $CaWO_4$ undoubtedly suggest a trapping of the electronic excitations in the forbidden energy gap of the crystal at a distance exceeding 1.5 eV from the bottom of the conduction band, most probably in the form of a relaxed exciton. This sounds reasonable at least for $CaWO_4$ considering the large Stokes shift (near 3 eV) of excitonic emission in this crystal [4]. The slower changes in the phase shift within the several picosecond time scale may reflect the exciton relaxation processes at oxyanionic complexes, involving symmetry and configuration changes in relative positions of oxygen and tungsten nuclei. The very small phase shifts observed in the $CdWO_4$ crystal probably indicate that the relaxed excitaton state is situated near 1.5 eV from the bottom of the conduction band.

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