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Contrasted Behaviour of an Electron Gas in MgO , Al_2O_3 and SiO_2 .

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Abstract. – We report on the observation, by use of a sub-picosecond time-resolved phase-sensitive technique, of an electron gas pumped by an intense femtosecond laser pulse into the conduction band of three different wide-band-gap oxides. The free-carriers lifetime is measured to be two orders of magnitude longer in MgO and in Al_2O_3 than in SiO_2 .

Understanding the processes leading from an electronic excitation to a lattice defect is a challenge of primary importance in insulating-material science. Time-resolved studies using high-intensity ultra-short laser pulses, which allow a direct access to the dynamics of the relaxation channels, have recently been carried out [1,2]. These investigations are pump-probe-type experiments aimed to observe the onset of an absorption band related to a lattice distortion. They bring fruitful information on the mechanism of intrinsic defects induced by electronic excitation. However, crucial questions cannot be answered directly with this technique, for instance what is the lifetime of the free carriers in the conduction band? This question is of fundamental importance because it addresses the problem of the electron trapping closely connected to the possibility for a given material to produce defects or not.

In this letter, we show that the direct, time-resolved, observation of the excited electrons provides new insights into such problems. This is demonstrated with the comparative study of three wide-band-gap oxides: magnesium oxide (MgO), alumina (Al_2O_3) and silica (SiO_2).

The principle of the experiment and the laser description have been given in detail elsewhere [3]. Let us just recall that the sample is probed by two twin laser pulses separated by a fixed time delay ($\Delta t = 3.6$ ps in the present set of experiments), one impinging the solid

before and the second after the pump pulse. The measured quantity is a phase shift in the interference pattern appearing in the frequency spectrum of the sequence of probe pulses. This phase shift, induced by the high-intensity pump pulse, is proportional to the modification of the refractive index, and its temporal evolution is obtained by changing the delay between the pump pulse and the two probe pulses. The laser pulses durations and wavelengths are, respectively, 70 fs and 310 nm (4.0 eV photons) for the pump beam, 60 fs and 560 nm (2.2 eV photons) for the probe beam. The overall experimental resolution is 120 fs. The pump beam is at normal incidence and the probe beam incidence angle is 45 degrees. The interaction region is imaged on the entrance slit of the spectrometer. The radial dimension is displayed along the slit, and the results presented in this paper are integrated along the radius of the pump beam. Perpendicularly, we select the part of the probe beam which crossed the pump beam closest to the sample surface (the first 100 μm). Thus, we avoid propagation effects such as beam filamentation, which occur deeper in the sample [4] and can be readily observed with the present experimental technique.

In fig. 1, 2 and 3, we present the measured variations of the phase shift (in radians) as a function of time for three different samples, Al_2O_3 , MgO and SiO_2 . For time delays close to zero, we observe a positive phase shift in both Al_2O_3 and in SiO_2 . As already detailed in [3], this positive phase shift is due to the phase modulation induced by the pump pulse and is present as far as the pump pulse and the probe pulse temporarily overlap. It is proportional to the product $n_2 I_p(t)$, where n_2 is the second-order non-linear index and $I_p(t)$ the time-dependent pump laser intensity. Note that we used a much lower pump laser intensity in MgO , therefore this initial positive phase shift is almost absent in fig. 2. Then, just after the pump pulse, the phase shift suddenly changes to negative values in the three materials. This reflects the presence of quasi-free electrons produced by multiphoton absorption from the valence band. Finally, *an extremely contrasted behaviour prevails for longer time delays: while the phase shift remains negative and almost constant in Al_2O_3 and in MgO (we attribute the observed fluctuations to the fact that each point is a single-shot measurement), it goes rapidly back to zero and then remains constant and positive in SiO_2* . As fig. 3 clearly shows, the time the electrons stay «alive» in the conduction band of $\alpha\text{-SiO}_2$ is very short (time decay of 150 fs) and their «annihilation» is attributed to the ultra-fast formation of E' centres [1, 3]. The last positive phase shift region is interpreted as the population of the E'

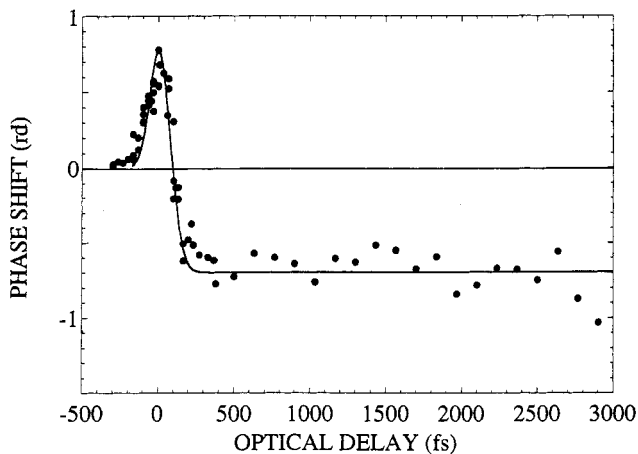


Fig. 1. – Phase shift for Al_2O_3 as a function of time. Dots: experimental data; full line: numerical simulation.

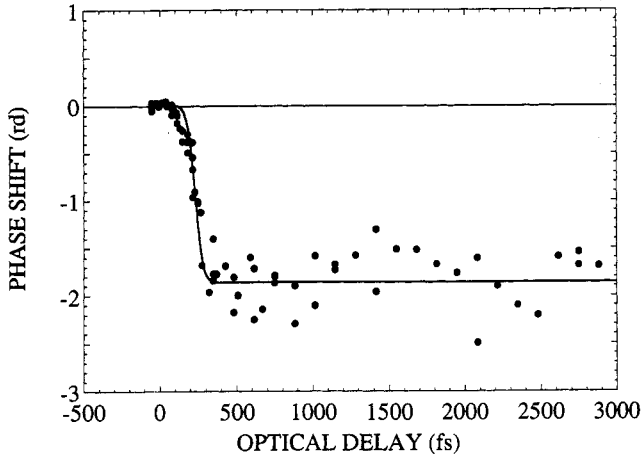


Fig. 2. – Phase shift for MgO as a function of time. Dots: experimental data; full line: numerical simulation.

centres which is constant (or decreases with a time constant much larger than measurable with this experimental set-up) for delays greater than 1 ps.

Let us analyse the above results from a more quantitative point of view by writing the phase shift between the two probe pulses as

$$\Delta\Phi(t) = 2\pi \frac{L}{\lambda} (n_a(t) - n_b(t)). \tag{1}$$

In the above expression, L is the effective length over which the index is modified ($70\ \mu\text{m}$), λ is the wavelength of the probe beam (560 nm), $n_b(t)$ and $n_a(t)$ are the index of the medium «seen», respectively, by the first (before the pump pulse) and the second (after the pump pulse) probe pulse. Of course, $n_b(t)$ is nothing but the usual refractive index (n_0), whereas $n_a(t)$ is the index of the medium perturbed by the pump laser beam. Considering a three-level system, namely the ground-state, the conduction band where the electrons are

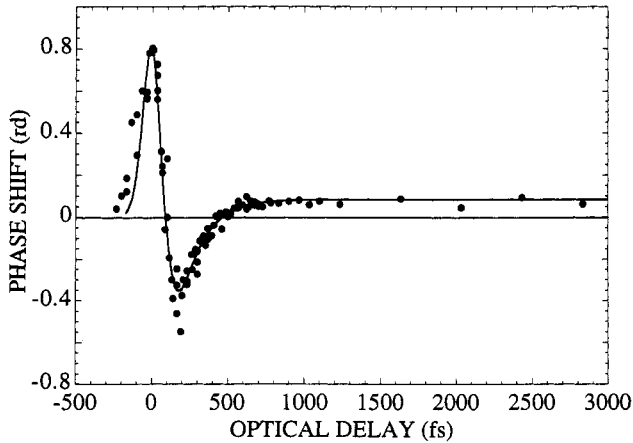


Fig. 3. – Phase shift for α -SiO₂ as a function of time. Dots: experimental data; full line: numerical simulation.

supposed to be free and a level in the band gap where the population can be trapped, we can express, starting with the general expression of the polarisation [5], the index of the medium as

$$n_a(t) = n_2 I_p(t) + \sqrt{n_0^2 - \frac{n_{cb}(t) e^2}{m_{cb}^* \varepsilon_0 \omega^2} + \frac{n_{tr}(t) e^2}{m_{tr}^* \varepsilon_0} \frac{1}{\omega_{tr}^2 - \omega^2}}. \quad (2)$$

In this expression, m_{cb}^* and m_{tr}^* are, respectively, the effective electronic masses in the conduction band (that we will assume equal to the free one) and in the trap level, ω is the probe laser frequency, ε_0 is the static dielectric constant of the material and e the electronic charge. ω_{tr} is the frequency corresponding to the maximum of the absorption band associated with the trap. The quantities $n_{cb}(t)$ and $n_{tr}(t)$ are the electron densities at a given time in the conduction band and in the trap level, respectively. For the sake of clarity, let us assume that the density of excited electrons is very small compared to the total electronic density (this is the case in the experiment). Using the first-order expansion of eq. (2), expression (1) becomes

$$\Delta\Phi(t) = 2\pi \frac{L}{\lambda} \left(n_2 I_p(t) + \left(\frac{1}{2n_0} \right) \left(-\frac{n_{cb}(t) e^2}{m_{cb}^* \varepsilon_0 \omega^2} + \frac{n_{tr}(t) e^2}{m_{tr}^* \varepsilon_0} \frac{1}{\omega_{tr}^2 - \omega^2} \right) \right). \quad (3)$$

The variation of the population is modelled by using a set of rate equations

$$\begin{cases} \frac{dn_{cb}(t)}{dt} = n_i \sigma^{(n)} I_p^n(t) - \frac{n_{cb}}{\tau_{tr}}, \\ \frac{dn_{tr}(t)}{dt} = \frac{n_{cb}}{\tau_{tr}}. \end{cases} \quad (4)$$

n_i is the initial valence electron density, $\sigma^{(n)}$ is the n -photon absorption cross-section where n is the minimum number of photons necessary to cross the band gap, $I_p(t)$ is the pump laser intensity, and τ_{tr} is the mean electron trapping time. The second term on the right-hand side of eq. (3) is proportional to the electron density in the conduction band and is always negative. Therefore, as previously mentioned, free electrons in the conduction band induce a negative phase shift. The sign of the third term depends on whether ω_{tr} is smaller or bigger than ω . In this last case ($\omega_{tr} > \omega$), i.e. if the energy necessary to excite the trapped electrons in a bond state in the band gap or in the conduction band is greater than the probe photon energy (2.2 eV), the presence of trapped electrons will induce a positive phase shift. Thus, if the mean trapping time is not infinite, the process must consist in the three phases observed in the case of SiO_2 . Note that our experiment does not allow to distinguish between quasi-free electrons and electrons trapped in levels very close to the bottom of the conduction band. Indeed, if $\omega_{tr} \ll \omega$ and if the effective masses are not notably different, the second and third terms in eq. (3) will contribute similarly to the phase shift.

The result of this model, applied to the three materials, is drawn in full lines in fig. 1, 2 and 3. Concerning the positive phase shift, we used the same value for the non-linear refractive index n_2 in Al_2O_3 and SiO_2 , namely $2 \cdot 10^{-16} \text{ cm}^2/\text{W}$. The experimental technique is sensitive and very well suited for measuring non-linear index. However, these values cannot easily be compared to the published one, since we are dealing with a phase modulation induced at a given frequency and probed at a different one. Our present results are close to previously published values, at least in SiO_2 [4].

From the negative part of the phase shift, we can directly deduce that the achieved excitation density is $0.7 \cdot 10^{19} \text{ cm}^{-3}$ in Al_2O_3 , $1.4 \cdot 10^{19} \text{ cm}^{-3}$ in MgO and $1.5 \cdot 10^{19} \text{ cm}^{-3}$ in SiO_2 .

The excitation process is the three-photon absorption in Al_2O_3 and in SiO_2 [6], since the band gap of these materials is larger than 8 eV, while absorption of two photons is enough to cross the band gap of MgO . Indeed the intensity used in the experiment was much smaller for this material ($8.7 \cdot 10^{11} \text{ W/cm}^2$ instead of $1.3 \cdot 10^{13} \text{ W/cm}^2$). The best fit is obtained with the following multiphoton cross-sections: $\sigma^{(3)} = 5 \cdot 10^{-84} \text{ cm}^6 \text{ s}^2$ in Al_2O_3 , $\sigma^{(3)} = 3 \cdot 10^{-84} \text{ cm}^6 \text{ s}^2$ in SiO_2 , and $\sigma^{(2)} = 6 \cdot 10^{-51} \text{ cm}^4 \text{ s}$ in MgO .

Concerning the temporal evolution of the phase shift in MgO and Al_2O_3 for longer time delays ($> 300 \text{ fs}$), we can assert, in the context of the model proposed above, that the electron population, if trapped, lies in levels no deeper than the photon energy. Its mean trapping time can be measured by letting the two probe pulses propagate through the sample after the pump pulse. Thus, they both experience a disturbed dielectric constant and the measured phase shift is proportional to the variation of the refractive index during the time delay that separates the two pulses. By using this relative mode measurement, we can increase the time delay between the pump pulse and the two probe pulses. The main time for the decrease of the excitation density was found to be 50 ps in MgO and 100 ps in Al_2O_3 , with an uncertainty of the order of 10%. We have assumed in the model that the trap energy was zero. The same result could be obtained assuming that the mean trapping time (into deep states) is quasi-infinite. The agreement between experimental data and the simulation is quite good and this is true until $\omega_{\text{tr}} \ll \omega$. Although we do not know exactly the position of these supposed levels and, more importantly, their exact nature, we can assert that this electron gas is very polarisable for optical frequencies and presents a plasma-like behaviour during a very long time compared to SiO_2 . Such shallow traps could be the so-called small polaron [7] which is, as is well known, the result of the «dressing» of the electron by the phonon field. More experiments are necessary to investigate this point and possibly reveal more subtle differences between different oxides.

Moreover, as already mentioned, the behaviour of SiO_2 is quite different. The mean trapping time has been taken to be 150 fs. The maximum of absorption for the E' centre (ω_{tr}) corresponds to a frequency of 5.7 eV [1, 8]. The unknown quantity is the effective mass of the electrons in the trap level which needs to be adjusted, since it is the only free parameter allowing to fit the positive phase shift. The best result has been obtained for a mass equal to three times the free one. We can observe that the population of E' centres remains, at such time scale, almost constant, in agreement with [1].

One could be surprised at such differences between amorphous SiO_2 (the result is the same for α -quartz as shown in [3]) and the other two materials MgO and Al_2O_3 because at first sight their linear optical properties are very similar. However, in SiO_2 , the existence of self-trapped excitons proves without ambiguities that in this material the electron-lattice coupling is very strong, making it unique among wide-band-gap oxides [9]. The electron-lattice coupling was reported to be weaker in MgO and Al_2O_3 [10], on the other hand known to be much more radiation-resistant than SiO_2 . However, the strength of the coupling between electrons and lattice is not enough to explain the propensity for a given material to produce defects under laser excitation. It is also necessary that the amount of energy stored in an electron-hole pair is high enough to displace an oxygen atom from its equilibrium position in the lattice, taking into account the fact that electrons are injected in our experiment near the bottom of the conduction band. To our knowledge, there is no available data on the energy needed to create a close Frenkel pair in SiO_2 . It is most likely intermediate between the energy needed to break two Si-O bonds, recently measured to be 6.8 eV [11], and the displacement energy for the oxygen, which is of 20 eV in SiO_2 [12], and therefore could be less than the band gap energy, as our results and those of Saeta and Greene [1] lead to anticipate. The displacement energies for the oxygen in Al_2O_3 and MgO are substantially higher (respectively 70 and 53 eV [12]). Without being a definite explanation, these figures are at

least consistent with the behaviour of the photoinjected electrons that we observe in this experiment. It is also worth noting that at low temperature, luminescence bands at wavelength closely corresponding to the band gap energy have been observed in MgO (excited by high-energy electrons) [13] and in Al_2O_3 (submitted to X-ray excitation) [14]. In SiO_2 , however, the very large Stoke shift observed in the low-temperature luminescence is one of the signature of the trapping of electron-hole pairs [9, 15]. This relaxation channel is quenched at room temperature in SiO_2 , but persists in MgO, indicating that radiative recombination is still an important, and maybe dominant, channel of relaxation in this material. To our knowledge, no luminescence study have been performed for Al_2O_3 at room temperature, but the similarity of our result for this material and MgO seems to exclude the last possible explanation for our data in these two materials, which is an extremely slow trapping into deep states.

In this paper, we have observed for the first time the temporal evolution of an electron gas pumped in the conduction band of three wide-band-gap insulators with a temporal resolution of 120 fs. We have shown that in contrast with $\alpha\text{-SiO}_2$, where the electron population is trapped in an extremely short time in levels associated with E' centres, the situation is extremely different in MgO and Al_2O_3 . In both these materials, the electronic gas remains highly polarisable at optical frequencies for more than 50 ps. These different behaviours correlate with the strength of the electron coupling, known to be exceptionally strong in SiO_2 , and also with the anion displacement energy. It is particularly worth noting that there is also a correlation of the behaviour of the free electrons in these three oxides with their resistance to radiolysis, much higher for Al_2O_3 and MgO than for SiO_2 . Whether this is a general result or not, more work is certainly needed to ascertain this point.

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