Time resolved study of carrier relaxation dynamics in α-Al_2O_3.

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Abstract : The relaxation of excited carriers in α-Al_2O_3 is complex, depending for instance on the type of ionizing radiation. Using femtosecond time-resolved absorption spectroscopy, we can induce a controllable excitation density on a wide range, and follow the relaxation dynamics from 30fs to 7ns. We show that the excited carrier decay is non-exponential: it is dependent on the pump intensity, i.e. on the initial carrier concentration. We describe the relaxation as a two-steps process, involving the trapping of initially free electron-hole pairs, followed by recombination. A numerical model taking into account the initial electronic excitation by multiphoton absorption and the subsequent relaxation allows to quantitatively reproduce the amplitude of the measured absorption and its temporal evolution.

Understanding the dynamics of excited carriers in wide band gap materials is a requirement to describe a broad range of physical mechanisms such as scintillator response, radiation induced damage of crystals, or laser-induced breakdown in optical materials and coatings. Due to its importance in various applications, the recombination of carriers in sapphire (α-Al_2O_3) has been studied using various excitation tools: electron pulses [1-3], VUV photons [4] and heavy ions [5]. The most recent works have shown that the decay of carriers, measured either by fast luminescence [5] or transient absorption [3] depends on the excitation conditions. The common feature of all these studies is that the initial excitation condition is not known, due to a complex and inhomogeneous cascade of relaxation following the excitation by high energy particles, obscuring the relaxation dynamics. In this work we address this issue by exciting the solid with ultrashort laser pulses and probing its subsequent evolution by measuring the transient absorption in wide spectral range. Indeed, ultrashort laser pulses are ideal tool for this kind of purpose since they altogether allow to induce a large excitation density without damaging the sample, and provide a temporal resolution high enough to track in real time the carrier dynamics, even in the case of non-radiative relaxation. By changing the energy of the impinging pulse, we can control and tune the initial carrier concentration and are in position to study the influence of this parameter and finally, to reveal the intrinsic relaxation mechanisms.

In the present work we use the second harmonic (400 nm) of an amplified Titanium-Sapphire laser (Coherent Libra) radiation which delivers 30 fs pulses with energy up to 5 mJ, at 1 KHz to excite the samples. To probe the absorption spectrum and its evolution, a small fraction of the main beam, passing through a delay line, is mildly focused in a CaF_2 crystal to generate a white light continuum. This probe beam is then focused onto the sample with a 15 cm focal length parabolic mirror. The pump beam is focused with a 40 cm lens 1 or 2 cm behind the sample. Its diameter is measured *in-situ* with a knife-edge method to be 203 µm (FWHM), enough to ensure a complete overlap with the probe beam. The probe beam is imaged at the entrance of a monochromator and red with a photodiode array. The optical density is deduced from the ratio of the intensity of the probe beam spectra measured with pump beam on and off, the latter being modulated at 500 Hz with an optical chopper. The samples are z-cut single α-Al_2O_3 plates with dimensions 10*10*1 mm. They are mounted on a x-y translation stage and continuously displaced to avoid cumulative damage. We have checked with an optical microscope that at the highest fluence used during the experiments, no apparent damage had been induced during the measurement, which was not the case if irradiation was taking place at a the stationary fixed position of the sample. The transient absorption spectra were measured for different probe delays in the range 1 ps to 1 ns after the excitation and are displayed in figure 1. Although measured in a narrower range, the spectra shows the same trend as the one reported recently by Koshimizu and coworkers [3]: after excitation with electron pulse or femtosecond laser, they observe a very broad absorption band, extending at least from 350 to 800 nm, with a maximum at 610nm. The similarity of absorption band obtained with different type of ionizing radiation strongly suggest an intrinsic initial electronic excitation, i.e. from valence band to conduction band. In our experiment carriers are excited by the simultaneous absorption of three photons (3.15 eV). Indeed the optical band gap of α-Al_2O_3 was measured to lie in the range 9.2 to 9.3 eV [6], and the threshold for generation of exciton was measured to be 8.8 eV [7]. At the pump intensity used in our measurement (13.4 to 26.8 TW/cm^2) it is well known that multiphoton process can efficiently excite a large density of carrier in wide band gap dielectrics [8, 9]. After absorption of three photons, only the lowest level of the conduction band is populated. Recent calculations of the electronic band structure in α-Al_2O_3 show that the two

lowest bands of the conduction band are separated by 1.5 eV [10,11] to 2.9 eV [12] The maximum of absorption observed around 2 eV is thus most probably due to transition between these two lowest levels of the conduction band.

It should be noted that the spectrum slowly evolves as time proceeds, and that a shoulder appears in the blue side of the spectrum, around 500 nm. The possible origin of this modification is discussed later. In figure 2, we have reported the time evolution of the absorption measured at the maximum, i.e. at 610 nm, as a function of time delay between pump and probe, and for three different fluences of the exciting pulse. The most obvious observation is that the decay is non exponential and strongly depends on time and initial intensity or density. This kind of observation of complex decay has already been reported [3,5], but not explained. Our interpretation is that the electron-hole recombination is following a *bimolecular* type kinetics. In other words, after creation of an electron hole pair - in our case by multiple photon absorption through the band gap - carriers are supposed to be very mobile as indicated by the measurements of Shan et al. in the TeraHertz domain [13]. Consequently, we assume that any electron can recombine with any hole. With this assumption, the higher the initial excitation density, the faster the recombination. This is most probably why, when measuring the temporal profile of luminescence [5] after excitation with high energy ions, it was observed that the decay is getting faster when using ions with higher linear energy transfer. Such acceleration of luminescence can also be attributed to interaction between excitons [14]. In this case the fastening of luminescence results from a competition between two different relaxation channels: radiative recombination, and a density dependent Auger type interaction between exciton. However this modification of decay appearing at high density is linked to a quenching of the luminescence, which is not observed in the case of α-Al_2O_3 [5].

Our first attempt to use a simple bi-molecular type of kinetics did not allow to reproduce the decay curves and was not successful. In order to account for the main experimental observations, and, at the same time, to keep the number of variable parameters to a minimum, we have devised the following two-step model: electron-hole pairs form excitons (or self-trapped excitons [1]) following a bimolecular kinetics, and these excitons will then recombine with a constant decay. This model is consistent with previous observation showing that an intrinsic radiative recombination – peaking at a photon energy of 7.8 eV, follows, at low temperature, excitation by VUV photons or heavy ions. This radiative recombination exhibits a narrow excitation spectrum centered at 8.8 eV, this means that excitons in Al_2O_3 are weekly bonded, with a small stoke shift of less than 1 eV. This is why the term of soft-self trapped excitons has been used in the case of Al_2O_3 [4].

In the framework of this model, the evolution of the different populations can be described with the following rate equations:

$$\frac{\partial \rho_{cb}(z,t)}{\partial t} = N_v \sigma_3 I^3(z,t) - \sigma v\, \rho_{cb}^2(z,t)$$

$$\frac{\partial \rho_{ste}(z,t)}{\partial t} = \sigma v\, \rho_{cb}^2(z,t) - \frac{\rho_{ste}(z,t)}{\tau_{rec}}$$

In these equations, ρ_{cb}, ρ_{vb} and ρ_{ste} are the populations of electrons in the conduction band, in the valence band and excitonic states, respectively. As already mentioned, the electron-hole pairs are excited by a 3 photon process, with a rate proportional to the third power of the pump laser intensity ($I^3(z,t)$) and to the 3-photon absorption cross section σ_3. Electron-holes then

form loosely bond excitons with a rate proportional to an electron-hole capture cross section σ and to the velocity of carriers v (we assume that the population of free electrons and free holes are equal at any time, hence the term ρ_{cb}^2). Finally, excitons recombine with a fixed lifetime τ_{rec}.

In addition, we calculate the absorption with the help of the dielectric function described by a Drude-Lorentz model:

$$n^2 - 1 = \frac{e^2}{m_e \epsilon_0} \frac{\rho_{vb} f_{12}}{\omega_g^2 - \omega^2} + \frac{e^2}{m_e \epsilon_0} \frac{\rho_{ste} f_{ste}}{\omega_{ste}^2 - \omega^2 - \frac{i\omega}{\tau_{ste}}} - \frac{e^2}{m^* \epsilon_0} \frac{\rho_{cb} f_c}{\omega^2 + \frac{i\omega}{\tau_{coll}}} + \chi_{3,eff} \mathcal{E}^2$$

The first three terms on the right side represent the usual dielectric function, which is perturbed by the presence of self-trapped excitons (described by second term) and excited free carriers (described by third term). Fourth term corresponds to optical Kerr effect. In this formula assumption is made that optical properties of free carriers and excitons are similar. Moreover, we have to take into account the initial spatial distribution of carriers along the propagation axis and the beam radius, since each initial local excitation density gives rise to its own local decay kinetics. Thus the spatial and time distribution of the pump beam is calculated by taking into account the damping due to multiphoton excitation as well as the absorption by the plasma. Finally the results of this model are shown by the full lines in figure 2 (time evolution of the absorption for different pump laser fluence), and figure 3 which displays the absolute amplitude of absorption for all the intensities used in the experiment. The agreement is quite satisfactory for the initial amplitude of absorption (figure 3), validating the hypothesis of a three photon excitation process in a wide range of initial excitation density, giving rise to optical density varying by more than 2 orders of magnitude. In Figure 3 we have also plotted a curve (dashed line) displaying the evolution of the absorption assuming a three photon process, i.e. a third power dependence of the signal. The difference between this curve on one side, and the result of the model and data points on the other side, is due to the depletion of the pump beam. The depletion effect increases with pump intensity, since the efficiency of the multiphoton process and the absorption due to the plasma are both increasing. The decay kinetics is also well reproduced by the model, the best agreement was obtained with the following parameters: $\tau_{rec} = 100 \pm 10$ps, with a value for the product $\sigma v = (1{,}35 \pm 0{,}1) \times 10^{-14}$ m^3/s. This corresponds to an electron capture cross section by holes of about 10^{-18}cm^2 if one assumes that electrons have a kinetic energy equal to the energy of one optical phonon (150 meV). Here also in figure 2 the output of the model are in good agreement with the experimental results, although a small discrepancy can be observed at intermediate times, around 1 ns. An improvement of the model would be possible by taking into account the distribution of electron kinetic energies in the valence band. Indeed this factor influence the recombination rate which depends on the velocity of carriers. Since the laser pulse does create a distribution of excitation in the conduction band which is getting broader when the intensity is increased. This could be taken into account in the simulation by using a set of rate equations for different electronic levels in the conduction band. However we believe that the expected improvement does not worth the noticeable increase of calculation time, and we preferred keeping a simple model with less parameters. Moreover we expect that the cooling of carriers is occurring on short time scale – of the order of a few ps, due to high electron-phonon collision rates [13] and that the initial high energy carrier distribution is rapidly cooled down via collisions with the lattice. Another

possible improvement could be to take into account different optical absorption bands for free electron-hole pairs and self-trapped excitons. At long probe delays we have seen that the absorption spectrum is slightly evolving, showing an increase of the blue side of the spectrum. We have reported on figure 4 the evolution of the population of free electron-hole and self-trapped exciton as a function of time. It should be noted that the two populations start to differ noticeably around 1ns after excitation, i.e. in the range where the absorption spectrum is also changing. This could indicate that the difference in absorption spectra reflects the change of population in the different levels.

To conclude, we have shown that generation of a controlled excitation density with variable intensity ultrashort laser pulses, in combination with time-resolved studies can bring valuable information to understand the carrier dynamics in wide band-gap materials. Thus, we could measure the absorption spectra and the decay dynamics in a broad range of initial excitation densities, in a time window going from 50 fs to 8 ns. We have developed a simple two step model, showing that electron hole pairs first form soft self-trapped excitonic states before recombining. Our model is general and also able to explain the fastening of luminescence decay observed when ions possessing higher linear energy transfer, i.e. inducing larger excitation density, are irradiating Al_2O_3 samples [5]. As pointed out by Koshimizu and co-authors, this fastening is not due to luminescence quenching, since the efficiency is also higher, therefore we believe it is most probably due, like in our case, to a faster exciton formation.

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Figure captions:

Figure 1: Normalized absorption spectra measured in crystalline α-Al_2O_3 1 ps, 10 ps, 100 ps and 1 ns after excitation of the sample by a 30 fs laser pulse at 400 nm with flux 280 mJ/cm^2. The maximum absorption is at 610 nm. It corresponds to an induced optical density of 0.3 at delay 1 ps and goes down to 0.17 after 1 ns.

Figure 2: Time evolution of the induced optical density (O.D.) at 610 nm in α-Al_2O_3 following excitation by a 30 fs laser pulse at 400 nm with different fluences: 860 (black), 645 (red) and 430 (red) mJ/cm^2: dots correspond to experimental data, and full lines to numerical simulation (see text).

Figure 3: Initial optical density immediately after excitation for different incident pump laser intensities: dots: experimental data, full line: simulation, dashed line: simple third order evolution described by $f(E) = aE^3$, E being the pump pulse energy and a free parameter taken such that this function passes through the first experimental point.

Figure 4: Evolution of the population of the two levels considered in the simulation: free electron hole pairs (dashed line) and excitons (full line), as a function of time, for all three fluences considered in this paper. The inset graph is a zoom in the early delays region.

Figure 1:

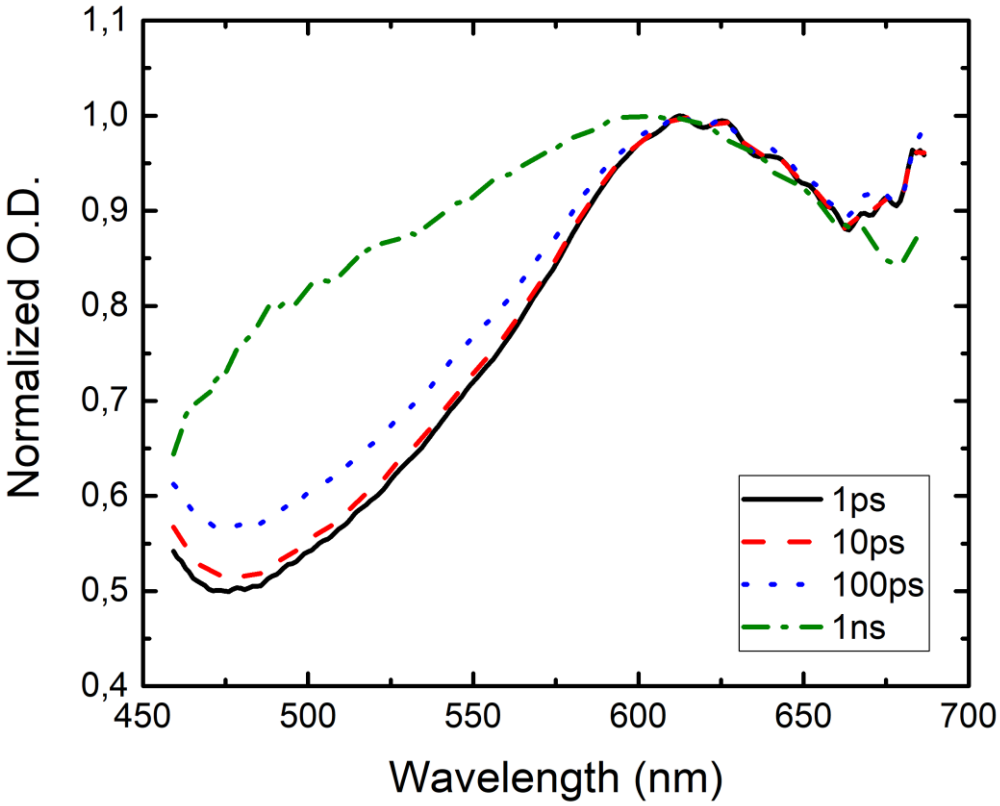

Normalized O.D.
1,1
1,0
0,9
0,8
0,7
0,6
0,5
0,4
450
500
550
600
650
700
Wavelength (nm)
1ps
10ps
100ps
1ns

Figure 2:

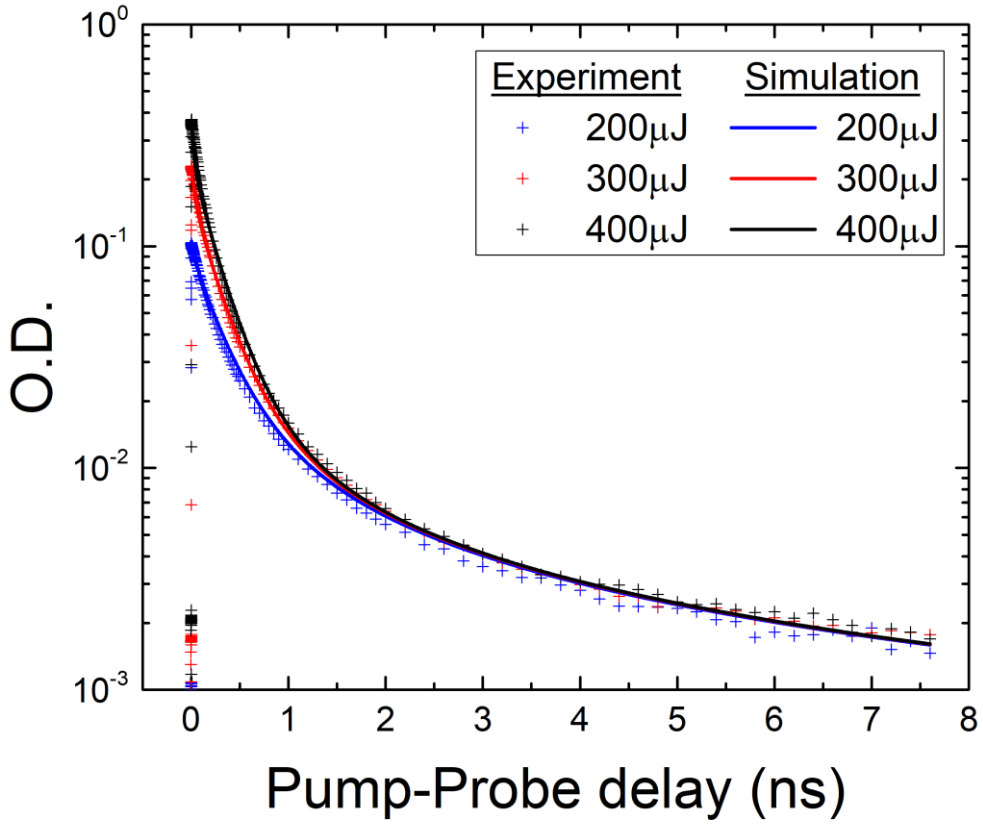

Experiment
Simulation
200μJ
300μJ
400μJ
200μJ
300μJ
400μJ
O.D.
Pump-Probe delay (ns)
10^0
10^-1
10^-2
10^-3
0
1
2
3
4
5
6
7
8

Figure 3:

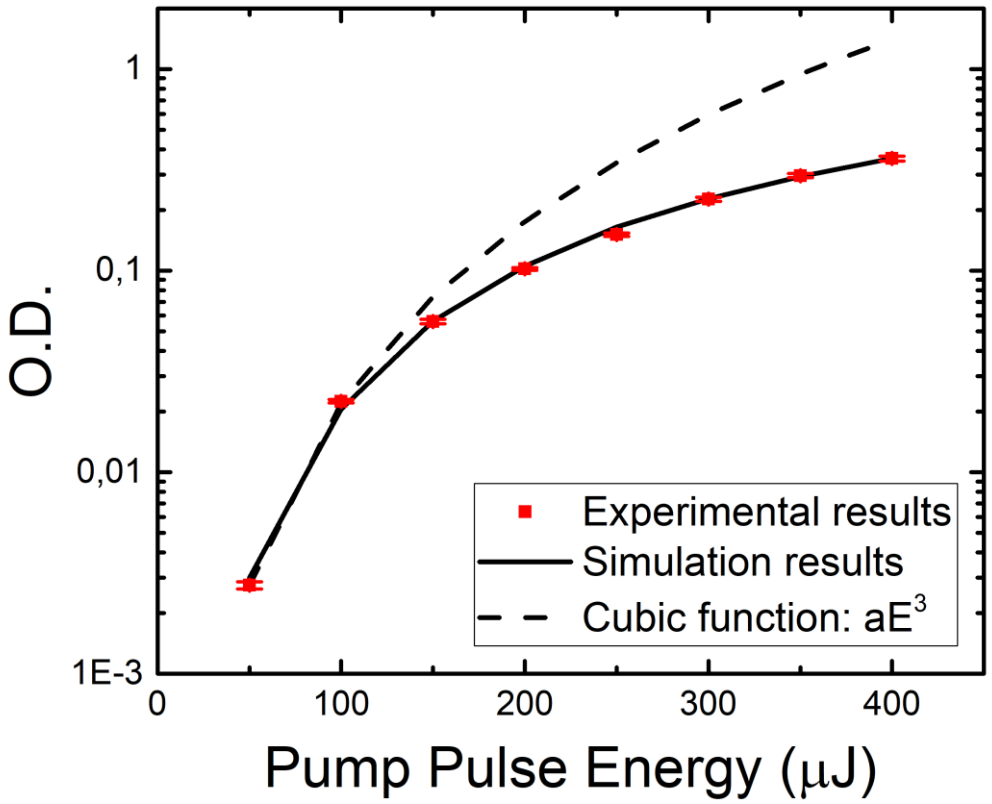
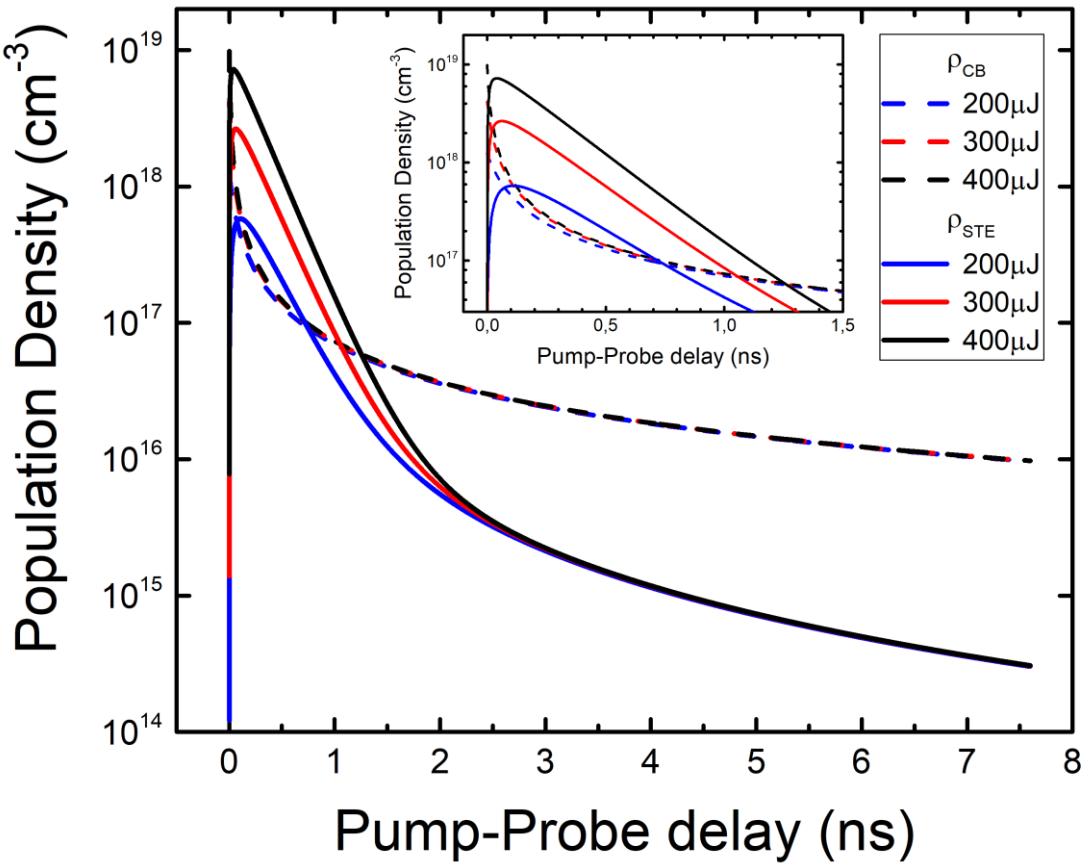

O.D.
1
0,1
0,01
1E-3
0
100
200
300
400
Pump Pulse Energy (μJ)
Experimental results
Simulation results
Cubic function: aE3

Figure 4:


Population Density (cm-3)
Pump-Probe delay (ns)
ρCB
200μJ
300μJ
400μJ
ρSTE
200μJ
300μJ
400μJ
Population Density (cm-3)
Pump-Probe delay (ns)