

# Visualization of the Multi-Center Ultrafast Response in Photoexcited Spinel Co<sub>3</sub>O<sub>4</sub>

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**Abstract:** Femtosecond optical and X-ray measurements show excitation-specific ultrafast relaxation processes in spinel Co<sub>3</sub>O<sub>4</sub> thin films. Upon ligand-to-metal and metal-to-metal charge transfer, the system decays through different energy pathways characterized by different coherent and incoherent responses. © 2022 The Author(s)

## 1. Introduction

Transition metal oxides (TMOs) represent promising materials for photovoltaic and photocatalytic applications because of their abundance, stability and band gap tunability [1]. Most technological applications rely on exploiting the photocarriers generated upon above band gap excitation, but the microscopic mechanism involved in their relaxation dynamics is often unclear. The complexity of the photoresponse in these systems arise from the correlated interaction of nuclear, spin and electronic degrees of freedom, due to the intermediate ionic character of the metal-oxide chemical bonds and the presence of partially filled d-orbitals localized on the metal centres.

In the past years, spinel Co<sub>3</sub>O<sub>4</sub> emerged as an excellent candidate for solar energy conversion and water splitting applications [2]. This system is a prototypical case of the intrinsic complexity of TMOs, due to its lattice and electronic structure: it has a normal spinel structure where Co<sup>2+</sup> and Co<sup>3+</sup> centres are surrounded by O<sup>2-</sup> anions and respectively occupy tetrahedral and octahedral sites with a 1:2 stoichiometric ratio. The electronic configuration of the metal centres, characterized by paired and unpaired d-electrons, determines the presence of Mott-Hubbard and charge transfer gaps close in energy. As a result, Co<sub>3</sub>O<sub>4</sub> has a rich optical spectrum with four bands peaked at 440 nm, 745 nm, 1320 nm, 1500 nm, respectively assigned to [3]: ligand-to-metal charge transfer (LMCT) from Oxygen to Cobalt centres; metal-to-metal charge transfer (MMCT) transition from Co<sup>3+</sup> to Co<sup>2+</sup>; a reversed MMCT process from Co<sup>2+</sup> to Co<sup>3+</sup>; a ligand field *d-d* transition localized on the Co<sup>2+</sup> centre.

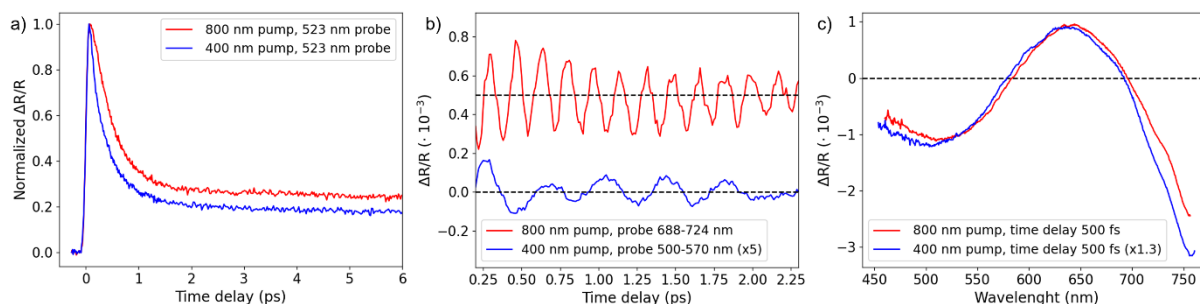
Even though few time-resolved investigations were performed to clarify some aspects of the Co<sub>3</sub>O<sub>4</sub> photodynamics [4,5], details on the sub-ps ultrafast relaxation of the light-activated system are still missing. From a fundamental standpoint, these steps are the most relevant as they govern the mechanism that brings the photogenerated charge carriers from above band gap excitations up to the low-lying *d-d* states of the Mott-Hubbard gap.

## 2. Methods

Femtosecond broadband transient reflectivity measurements were performed with a custom-made set up [6] on a 27 nm spinel Co<sub>3</sub>O<sub>4</sub> thin film. The sample was epitaxially oriented along the (111) direction and deposited on a (0001) sapphire (Al<sub>2</sub>O<sub>3</sub>) substrate by pulsed laser deposition. The film was excited at 10 kHz with the laser fundamental at 800 nm and at 400 nm, obtained by frequency doubling the 800 nm light with a type I  $\beta$ -barium borate (BBO) crystal, and probed on a shot-to-shot basis with a visible supercontinuum generated by a CaF<sub>2</sub> crystal (instrument response function <100 fs, 20 kHz repetition rate, pump fluence 0.5-1.5 mJ/cm<sup>2</sup>).

## 3. Results

Figure 1a shows the normalized time traces upon 800 nm (MMCT transition, red) and 400 nm (LMCT transition, blue) excitation and 523 nm probe. The curves are characterized by a biexponential decay and a constant offset, with time constants of  $\tau_1^{400nm} = 180$  fs and  $\tau_2^{400nm} = 590$  fs, and  $\tau_1^{800nm} = 410$  fs and  $\tau_2^{800nm} = 5.9$  ps, obtained through a global fit analysis. Figure 1b shows the mean value of the residuals in the probe ranges 688-724 nm (red) and 500-570 nm (blue), which correspond to the regions with the strongest coherent oscillations for 800 nm and 400 nm pump wavelengths, respectively. The MMCT excitation (red) stimulates a coherent phonon with a period of 170 fs (196 cm<sup>-1</sup>) presumably *via* an impulsive stimulated Raman scattering (ISRS) process [7], as it corresponds to the Raman active T<sub>2g</sub> mode of spinel Co<sub>3</sub>O<sub>4</sub> [8]. Conversely, the LMCT excitation (blue) leads to coherent oscillations of 407 fs (82 cm<sup>-1</sup>), which do not correspond to any Raman active mode of the system. As a consequence, we ascribe this process to a dispersive excitation of coherent phonons (DECP) [9].



**Figure 1:** Transient reflectivity measurements on  $\text{Co}_3\text{O}_4$ : (a) normalized time traces for 800 nm (red) and 400 nm (blue) excitation and 523 nm probe; (b) average residuals over the wavelength ranges 688-724 nm (800 nm pump, red curve) and 500-570 nm (400 nm pump, blue curve, scaling factor  $\times 5$ ); (c) energy traces at 500 fs time delay for 800 nm (red) and 400 nm (blue, scaling factor  $\times 1.3$ ) excitation wavelengths.

In Figure 1c we report the energy cut of the transient reflectivity maps at a time delay of 500 fs for 800 nm (red) and 400 nm (blue) pump wavelengths. The two traces are characterized by two negative features peaked around 520 nm and 750 nm, and a positive band centered around 640 nm. These line shapes are preserved up to the longest time delay that we investigated (800 ps).

Our results show that the energy cuts obtained in the visible region upon LMCT and MMCT excitation are degenerate, in agreement with a picosecond transient absorption and reflectivity study on  $\text{Co}_3\text{O}_4$  films, in which the samples were excited at 520 nm, 800 nm and 1400 nm [4]. The authors concluded that within few ps the system relaxes into the same low-energy  $d-d$  states, independently of the excitation wavelength. However, our findings demonstrate that different optical excitations trigger different responses of the system. In particular, the relaxation process upon 400 nm excitation is faster than the one at 800 nm, ruling out a stepwise relaxation cascade from the highest LMCT to the lowest  $d-d$  gap through the intermediate MMCT state. The presence of strongly different coherent responses for the two pump energies shows that band-specific relaxation pathways are mediated by different electron-phonon couplings. This idea is supported by our recent femtosecond X-ray emission spectroscopy (XES) measurements performed at the Femtosecond X-ray Experiments (FXE) scientific instrument of the European X-ray Free-Electron Laser (XFEL) [10], which show non-degenerate electronic and spin responses of the Cobalt centres at sub-ps time scales. The complexity of the  $\text{Co}_3\text{O}_4$  relaxation decay is confirmed by temperature-dependent transient reflectivity experiments across the antiferromagnetic phase transition of the system at 40 K, with the temperature strongly modifying coherent and incoherent transient reflectivity signals.

#### 4. Conclusions

In this work we demonstrated specific ultrafast photoresponses in  $\text{Co}_3\text{O}_4$  upon excitations of LMCT and MMCT transitions. Different coherent and incoherent relaxation dynamics are observed on sub-ps time scales, with the selective generation of DECP phonons and a faster decay of the optical signal upon 400 nm excitation. These results show the complexity of TMO systems and the opportunities for optoelectronic applications offered by multiband gap materials.

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#### 5. References

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