Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Investigation of Band Gap Narrowing in Nitrogen-Doped $La_2Ti_2O_7$ with Transient Absorption Spectroscopy

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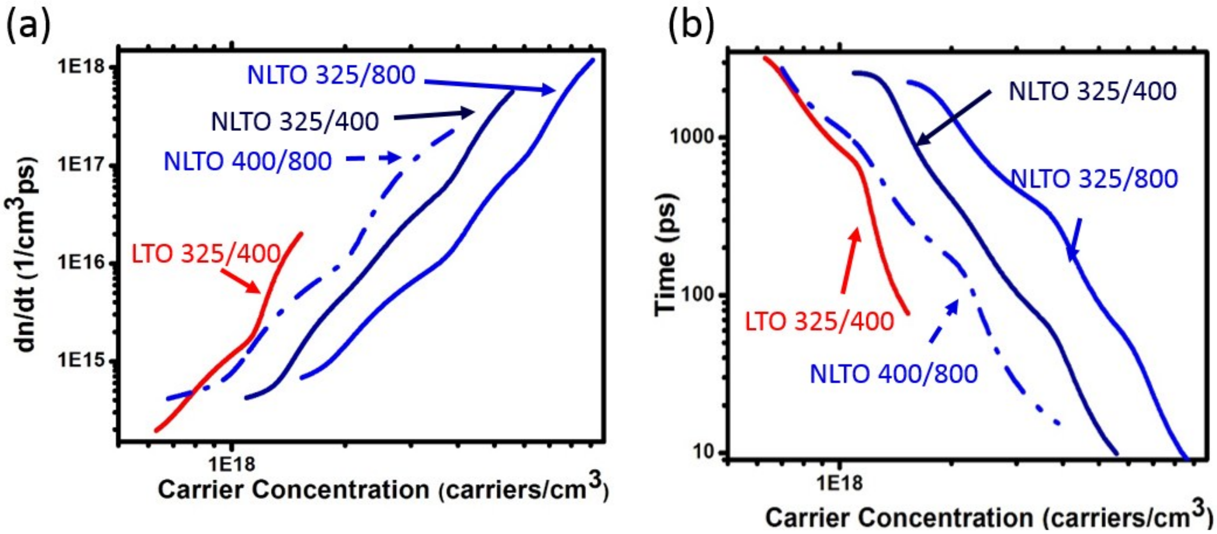

Figure S1. Inversion analysis of the transient absorption spectroscopy data. As discussed in Reference 24, this technique more accurately describes the underlying rate equation than an exponential fit alone. Each curve is labelled by two numbers, representing pump and probe wavelengths in nanometers respectively. (a) Rate $(\frac{dn}{dt})$ versus carrier concentration (n). (b) Carrier lifetimes.

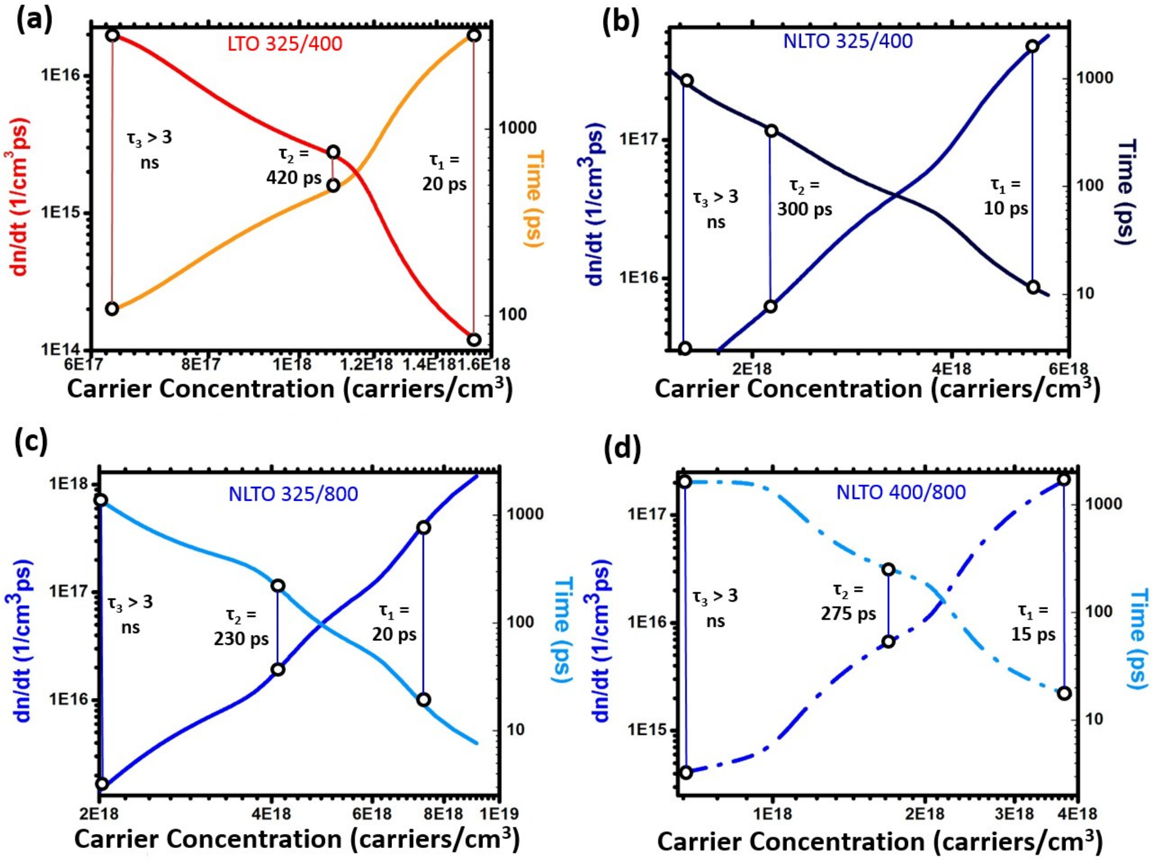

Figure S2. Inversion analysis of transient absorption. Each plot overlays the rate $(\frac{dn}{dt})$ and carrier lifetime (τ) versus carrier concentration (n). Each plot has three vertical lines, corresponding to the time constants from the exponential fits of Figure S1. Each vertical line depicts the carrier concentration at the fitted value of τ.

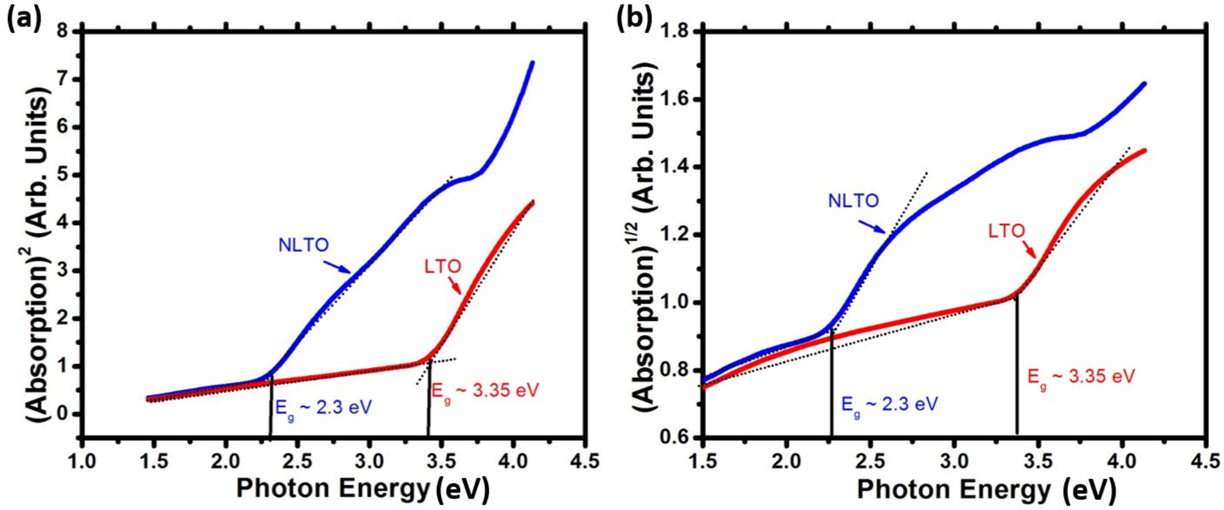

Figure S3. Tauc plots. Plotting photon energy versus (Absorption)^2 and (Absorption)$^{1/2}$ allowed for the shift in band gap to be experimentally confirmed. (a) When plotted as (Absorption)^2 versus photon energy the data was linear, showing that adding the nitrogen dopant shifted the band edge while maintaining direct transitions. The energy gap of intrinsic LTO was ~ 3.35 eV while the energy gap of NLTO was shifted to ~2.3 eV. (b) Plotting (Absorption)$^{1/2}$ versus photon energy represents indirect transitions. The data was not linear when plotted in this manner, showing that the transitions were not indirect before or after doping.

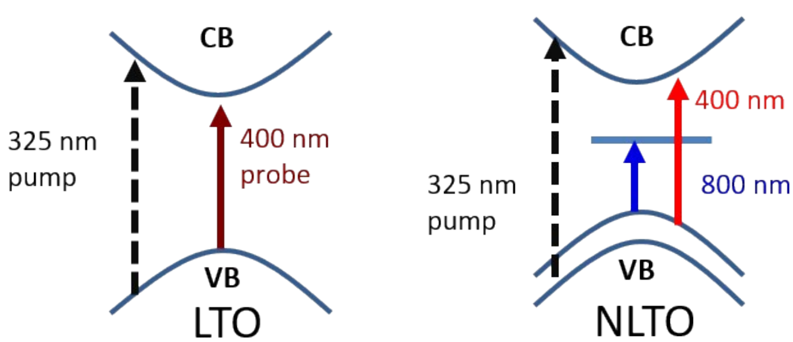

Figure S4. Band structure schematic. The schematic shows the transitions allowed by each pump and probe wavelength.

Table S1. Exponential fit coefficients. Each transient curve (Figure 3) was measured with resolution out to 3 ns, so any time constant greater than 3 ns could not be known within experimental uncertainty.

Sample and Pump/Probe Wavelengths (nm)	**τ_1 (ps)**	**τ_2 (ps)**	**τ_3 (ps)**	**Amplitude 1**	**Amplitude 2**	**Amplitude 3**
LTO 325/400	20	420	>3000	-6.4E-4	-1.3E-3	1.2E-3
NLTO 325/400	10	300	>3000	-9.2E-3	-5.7E-3	-2.8E-3
NLTO 325/800	20	230	>3000	-5.5E-3	-2.6E-3	-2.6E-3
NLTO 400/800	15	275	>3000	-3.0E-3	-2.3E-3	-9.2E-4

Table S2 The THz conductivity was fit to the following model after: C. Richter and C. A. Schmuttenmaer. *Nature Nanotechnol.*, 2010, **5**, 769-772.

$$\sigma(\omega) = \frac{\sigma_0}{1 - i\omega\tau}\left(1 + \frac{C}{1 - i\omega\tau}\right) + \frac{A}{\omega_0^2 - \omega^2 - i\omega\Gamma_{LD}}$$

The goal of the model was to find a few parameter fit to represent the shift in the zero frequency conductivity, including the resonance at ~1.8 THz. ω is in THz and the sign of C represents a Drude term (C=0) or a Drude-Smith model (C=-1) describing the influence of backscattering at interfaces.

	σ_0 $(\Omega m)^{-1}$	τ (1/THz)	C	A (THz²/ Ωm)	ω_0 (THz)	Γ_{LD} (THz)
LTO	3600	0.1	-1	400	1.78	0.4
N-LTO	10,200	0.1	-1	370	1.82	0.4