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Supplementary Information for

Spectral dynamics of shift-current in ferroelectric semiconductor SbSI

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Supplementary Information Text

Effective THz generation length and shift distance

The dynamics of shift current $J_{\mathrm{shift}}(t)$ was calculated by convoluting the incident laser intensity $I(z,t)$ and the derivative of one-photon charge-shift $e\frac{d}{dt}r_{\mathrm{shift}}(t)$. Integrating along the depth (z) direction, the shift current reads

$$J_{\mathrm{shift}}(t) = \frac{1}{\hbar\omega_{\mathrm{exc}}}\int_{-\infty}^{\infty} e\frac{d}{dt'}r_{\mathrm{shift}}(t')I(z=0,t-t')dt' \ . \quad \text{[S1]}$$

After Fourier transformation, the THz pulse emitted outside the sample is

$$E^{\mathrm{emit}}_{\mathrm{shift}}(\omega) = -t^{\mathrm{sam}}_{\mathrm{THz}}t^{\mathrm{sam}}_{\mathrm{exc}}\frac{e}{\hbar\omega_{\mathrm{exc}}}\omega^2 r_{\mathrm{shift}}(\omega)I(\omega), \quad \text{[S2]}$$

where $t^{\mathrm{sam}}_{\mathrm{exc}}$ and $t^{\mathrm{sam}}_{\mathrm{THz}}$ are the transmission coefficients of the sample for excitation light and generated THz wave, respectively.

For the case of the reference ZnTe(110) crystal, the electric field induced by photoexcitation can be expressed as

$$\begin{aligned} E_{\mathrm{OR}}(\omega) &= -\omega^2\int_0^d P_{\mathrm{OR}}(\omega)\exp\left[i(n(\omega)+n_{\mathrm{g}})\omega-\alpha(\omega_{\mathrm{exc}})z\right]dz \\ &= -\omega^2 L_{\mathrm{OR}}(\omega)P_{\mathrm{OR}}(\omega), \quad \text{[S3]} \end{aligned}$$

where P_{OR} is the nonlinear optical polarization [1],

$$P_{\mathrm{OR}}(\omega) = \frac{\chi^{(2)}}{n^{\mathrm{ref}}(\omega_{\mathrm{exc}})c}I(\omega), \quad \text{[S4]}$$

with the refractive index $n^{\mathrm{ref}}(\omega_{\mathrm{exc}})$, speed of light c, thickness d, and absorption coefficient at the excitation energy $\alpha(\omega_{\mathrm{exc}})$. The effective generation length of optical rectification $L_{\mathrm{OR}}(\omega)$ comes from the phase matching condition;

$$L_{\mathrm{OR}}(\omega) = \left[\frac{\exp\left(\frac{i\omega}{c}(n_{\mathrm{g}}+n(\omega))d-\alpha(\omega_{\mathrm{exc}})d\right)-1}{\frac{i\omega}{c}\left(n_{\mathrm{g}}+n(\omega)\right)-\alpha(\omega_{\mathrm{exc}})}\right]. \quad [S5]$$

By assuming $\alpha(\omega_{\mathrm{exc}})=0$ and the nonlinear optical coefficient $\chi^{(2)}$ is constant within the laser band-width, we observe, at outside of the sample,

$$E^{\mathrm{emit}}_{\mathrm{OR}}(\omega) = -t^{\mathrm{ref}}_{\mathrm{THz}}t^{\mathrm{ref}}_{\mathrm{exc}}\frac{\chi^{(2)}\omega}{n^{\mathrm{ref}}(\omega_{\mathrm{exc}})\left|n^{\mathrm{ref}}_{\mathrm{g}}+n^{\mathrm{ref}}(\omega_{\mathrm{THz}})\right|}I(\omega)/2. \quad \text{[S6]}$$

Here $n^{\mathrm{ref}}_{\mathrm{g}}$ is group refractive index ($n^{\mathrm{ref}}_{\mathrm{g}} = n^{\mathrm{ref}}+\omega_{\mathrm{exc}}\frac{dn^{\mathrm{ref}}}{d\omega_{\mathrm{exc}}}$), and 1/2 comes from the symmetry of $\chi^{(2)}$ tensor of ZnTe.

Using this $E^{\mathrm{emit}}_{\mathrm{OR}}(\omega)$ as reference, we evaluate the $r_{\mathrm{shift}}(\omega)$ as

$$r_{\mathrm{shift}}(\omega) = \chi^{(2)}\frac{t^{\mathrm{ref}}_{\mathrm{THz}}t^{\mathrm{ref}}_{\mathrm{opt}}}{t^{\mathrm{sam}}_{\mathrm{THz}}t^{\mathrm{sam}}_{\mathrm{opt}}}\left(\frac{\hbar\omega_{\mathrm{exc}}}{e}\right)\frac{2}{i\omega n^{\mathrm{ref}}_{\mathrm{opt}}\left|n^{\mathrm{ref}}_{\mathrm{g}}+n^{\mathrm{ref}}_{\mathrm{THz}}\right|}\frac{E^{\mathrm{emit}}_{\mathrm{shift}}(\omega)}{E^{\mathrm{emit}}_{\mathrm{OR}}(\omega)} \quad \text{[S7]}$$

The inverse Fourier transformation of $r_{\mathrm{shift}}(\omega)$ gives $r_{\mathrm{shift}}(t)$.

The photocurrent spectrum for the in-gap OR (Fig. 2*C* in the main text) is normalized by the L_{OR} assuming that the excitation photon density is constant throughout the sample (negligible photon absorption). In contrast, the shift current spectrum is affected penetration depth $\frac{1}{\alpha(\omega_{\mathrm{exc}})}$. Thus, the appreciable THz intensity and current for the in-gap OR (Fig. 5 in the main text) are due to the integration of weak signals in the extended depth (L_{OR}) in the sample.

THz waveforms under varying excitation photon energy

Figure S1*A* and S1*B* show waveforms and its FFT spectra at 1.5-1.8 eV, and 2.1 eV excitation photon energy. The data for 1.5 to 1.7 eV excitations is expected to be free from photo-absorption, which show similar waveform and spectrum with those for 1.8 eV excitation, where the Urbach tail may extend from the band edge. This result supports that emission of THz wave at 1.8 eV excitation can also be ascribed to the in-gap optical rectification, without the effect of the Urbach absorption. We note that the defect states will not generate the shift current, because the Berry connection is not well defined.

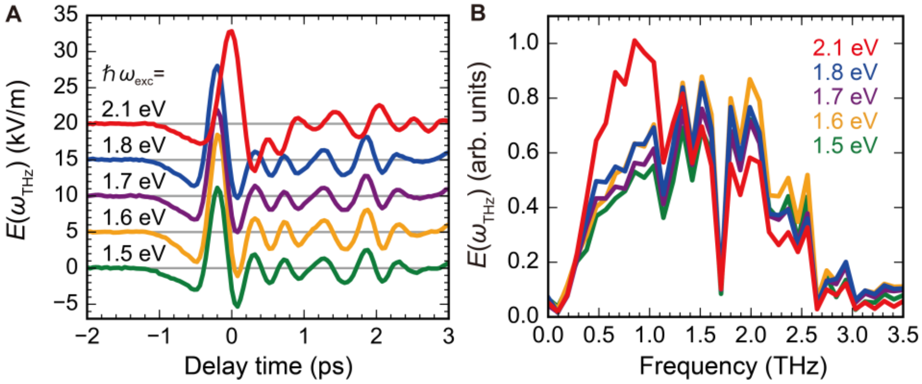

Fig. S1. Excitation photon energy dependence of THz waveforms ($E_{\mathrm{exc}} \parallel E_{\mathrm{THz}} \parallel c$, 282 K). (*A*) THz waveforms (offset for clarity). (*B*) Absolute amplitude spectra.

References

1. Schneider A, Neis M, Stillhart M, Ruiz B, Khan RUA, Günter P (2006) Generation of terahertz pulses through optical rectification in organic DAST crystals: theory and experiment. *J Opt Soc Am B* 23:1822-1835.