Supplementary Material for: Chalcophosphate Metasurfaces with Multipolar Resonances and Electro-Optic Tuning

Viktoriia E. Babicheva*[1] and Mariacristina Rumi[2]

[1]Department of Electrical and Computer Engineering, University of New Mexico, Albuquerque, New Mexico 87131, USA
[2]Air Force Research Laboratory, Materials and Manufacturing Directorate, Wright-Patterson AFB, Ohio 45433, USA

1 Additional Simulation Results

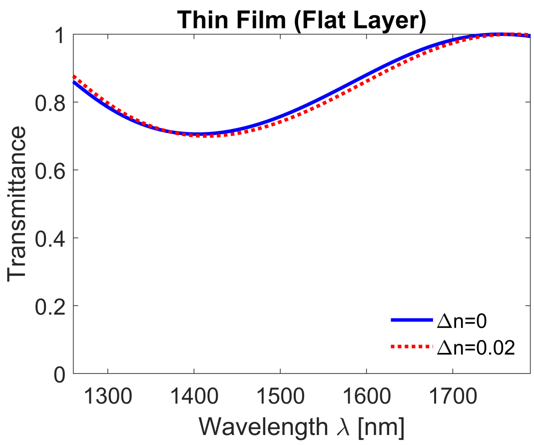
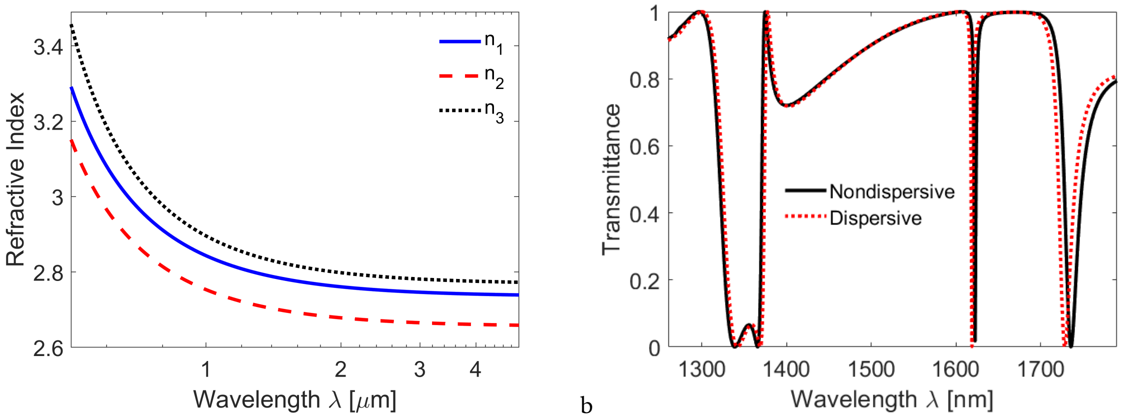


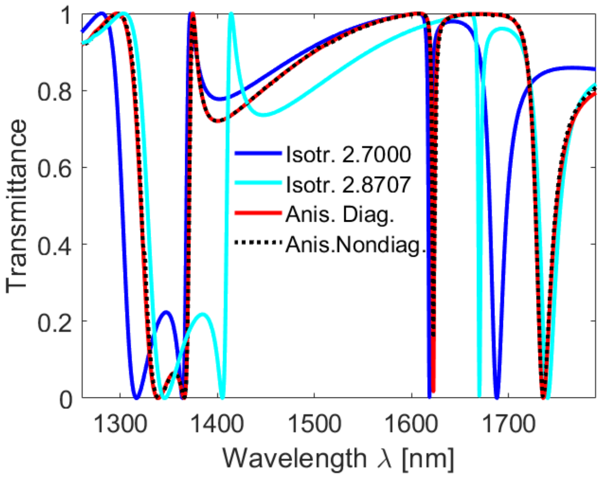
Figure S1: Transmittance of a thin film (continuous flat layer) of material with refractive index $n = 2.7$ and thickness of 650 nm, on a silica substrate. On top of the film, there is a superstrate with the same refractive index as the substrate. The solid line corresponds to the unbiased crystal ($\Delta n = 0$). The dashed line is for a biased crystal corresponding to an isotropic change in the refractive index $\Delta n = 0.02$. The ordinate axis is shown in the same range as in Figure 2a of the main text.

*vbb@unm.edu



a b

Figure S2: a Refractive index of $Sn_2P_2S_6$ reported in Ref. [1]. b Transmittance of a dense nanoantenna array without accounting for refractive index dispersion of $Sn_2P_2S_6$ (solid black line) and accounting for it (dotted red line). The antenna and array dimensions are the same as in Figure 2a of the main text.



a

	n_{xx}	$n_{yy} = n_{zz}$
MD+EQ		✓
ED+MQ	✓	
MOC+even	✓	
EOC+odd		✓

b

Figure S3: a Transmittance of a dense nanoantenna array under various approximations: (blue) isotropic material with $n_{xx} = n_{yy} = n_{zz} = 2.7000$; (light blue) isotropic material with $n_{xx} = n_{yy} = n_{zz} = 2.8707$; (red) anisotropic material with zero off-diagonal elements in the frame of reference of Figure 1a, with $n_{xx} = 2.7$ and $n_{yy} = n_{zz} = 2.8707$; (dotted black) anisotropic material with non-zero off-diagonal elements, with $n_{xx} = 2.7000$, $n_{yy} = n_{zz} = 2.8707$, and $n_{yz} = n_{zy} = 0.02081$. The optical properties of nanoantennas built from a material with off-diagonal refractive index components are simulated using the commercial software COMSOL, which allows for the account of arbitrary tensor components of n. b Table summarizing which resonance is mainly affected by the various components of the material tensor based on the results from panel a. It can be concluded that, while an array consisting of nanoantennas built from an anisotropic material would exhibit resonances at wavelengths different from those of a corresponding isotropic system, the nature of the modes and the overall spectral response are expected to be quite similar, and thus the modes can also be similarly modified by an applied field.

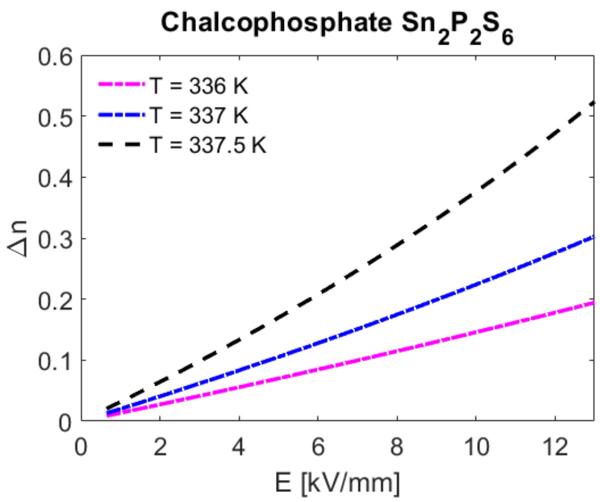


Figure S4: Maximum induced change in refractive index $|\Delta n|$ that can be achieved in $Sn_2P_2S_6$ as a function of bias E at three temperatures close to T_c, T = 336, 337, and 337.5 K. Taking into account r_{111}, for these temperatures, the EO coefficients are 1.37, 2.02, and 3.15 nm/V, respectively. These traces complement the results presented in Figure 4a of the main text and are based on the same set of experimental data from Ref. [1].

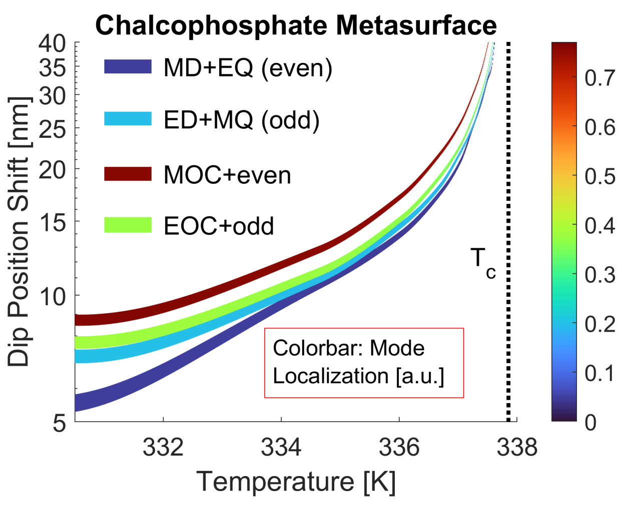


Figure S5: EO-induced shift of the dip position with respect to temperature T at fixed electric field. Simulations are performed for four modes of the dense array that forms chalcophosphate $Sn_2P_2S_6$ metasurface and the bias of E = 6.5 kV/mm. The calculations are the same as in Figure 4b of the main text, but relate to changes in r_{221} with respect to temperature and not bias. Note the logarithmic scale of the ordinate axis. The colorbar indicates the mode localization defined in the same way as in Figure 3 of the main text. Here, MD+EQ mode is analyzed for $a_x = a_y = a_z$ = 470 nm, ED+MQ for 550 nm, MOC+odd for 683 nm, and EOC+even for 716 nm. $D_x = D_y$ = 750 nm for all calculations of the dense array.

2 Multipolar Decomposition

The multipolar decomposition allows us to calculate the contribution of each multipole term to the overall response of the metasurface, and it uses the field distribution in the simulation domain to derive multipolar moments [2]. The multipolar decomposition method is based on the induced electric polarization $\mathbf{P}(\mathbf{r}) = \varepsilon_0(\varepsilon_p - \varepsilon_s)\mathbf{E}^{\text{ins}}(\mathbf{r})$, where $\mathbf{E}^{\text{ins}}(\mathbf{r})$ denotes the electric field within the nanoantenna. Here, ε_0 represents the vacuum permittivity, whereas $\varepsilon_p = n^2$ and $\varepsilon_s = n_s^2$ are the relative permittivity of the nanoparticle and the surrounding medium, respectively. We employ Cartesian multipolar representations based on spherical harmonic functions. The expressions for the multipolar moments are the following:

$$\begin{aligned}\mathbf{p} &= \int \mathbf{P} j_0(k_s r) d\mathbf{r} \\ &+ \frac{k_s^2}{10}\int \{[\mathbf{r}\cdot\mathbf{P}]\mathbf{r} - \frac{1}{3}r^2\mathbf{P}\}\frac{15 j_2(k_s r)}{(k_s r)^2} d\mathbf{r},\end{aligned} \tag{1}$$

$$\mathbf{m} = -\frac{i\omega}{2}\int [\mathbf{r}\times\mathbf{P}]\frac{3 j_1(k_s r)}{k_s r} d\mathbf{r}, \tag{2}$$

$$\begin{aligned}\hat{Q} &= \int \{3(\mathbf{r}\otimes\mathbf{P} + \mathbf{P}\otimes\mathbf{r}) - 2[\mathbf{r}\cdot\mathbf{P}]\hat{U}\}\frac{3 j_1(k_s r)}{k_s r} d\mathbf{r} \\ &+ 6k_s^2 \int \{5\mathbf{r}\otimes\mathbf{r}[\mathbf{r}\cdot\mathbf{P}] - (\mathbf{r}\otimes\mathbf{P} + \mathbf{P}\otimes\mathbf{r})r^2 \\ &- r^2[\mathbf{r}\cdot\mathbf{P}]\hat{U}\}\frac{j_3(k_s r)}{(k_s r)^3} d\mathbf{r},\end{aligned} \tag{3}$$

$$\hat{M} = \frac{\omega}{3i}\int \{[\mathbf{r}\times\mathbf{P}]\otimes\mathbf{r} + \mathbf{r}\otimes[\mathbf{r}\times\mathbf{P}]\}\frac{15 j_2(k_s r)}{(k_s r)^2} d\mathbf{r}, \tag{4}$$

$$\begin{aligned}\hat{O}^{(e)} &= 15\int \{\mathbf{P}\otimes\mathbf{r}\otimes\mathbf{r} + \mathbf{r}\otimes\mathbf{P}\otimes\mathbf{r} + \mathbf{r}\otimes\mathbf{r}\otimes\mathbf{P} \\ &- \hat{A}\}\frac{j_2(k_s r)}{(k_s r)^2} d\mathbf{r},\end{aligned} \tag{5}$$

$$\begin{aligned}\hat{O}^{(m)} &= \frac{-105 i\omega}{4}\int \{[\mathbf{r}\times\mathbf{P}]\otimes\mathbf{r}\otimes\mathbf{r} + \mathbf{r}\otimes[\mathbf{r}\times\mathbf{P}]\otimes\mathbf{r} \\ &+ \mathbf{r}\otimes\mathbf{r}\otimes[\mathbf{r}\times\mathbf{P}] - \hat{A}'\}\frac{j_3(k_s r)}{(k_s r)^3} d\mathbf{r},\end{aligned} \tag{6}$$

where k_s is the wavenumber in the surrounding medium, the integral is extended over the region where $\mathbf{P}$ is nonzero [3]. The notation $j_n(\rho)$ denotes the spherical Bessel function of the n-th order, and it is defined by $j_n(\rho) = \sqrt{\pi/2\rho}J_{n+1/2}(\rho)$, where $J_n(\rho)$ is the Bessel function of the first kind. The following expressions are used:

$$A_{\beta\gamma\tau} = \delta_{\beta\gamma}V_\tau + \delta_{\beta\tau}V_\gamma + \delta_{\gamma\tau}V_\beta, \tag{7}$$

$$V = \frac{1}{5}[2(\mathbf{r}\cdot\mathbf{P})\mathbf{r} + r^2\mathbf{P}], \tag{8}$$

$$A'_{\beta\gamma\tau} = \delta_{\beta\gamma}V'_\tau + \delta_{\beta\tau}V'_\gamma + \delta_{\gamma\tau}V'_\beta, \tag{9}$$

$$V' = \frac{1}{5}r^2[\mathbf{r}\times\mathbf{P}], \tag{10}$$

where $\beta = x,y,z$, $\gamma = x,y,z$, $\tau = x,y,z$, and $\delta_{\beta\gamma}$ is the Kronecker delta. The general expressions for the transmission coefficient, described by the multipolar moments for x-polarization, is:

$$\begin{aligned}t =& 1 + \frac{ik_s}{E_0 2S_L\varepsilon_0\varepsilon_s}(p_x + \frac{\sqrt{\varepsilon_s}}{c}m_y - \frac{ik_s}{6}Q_{xz} \\ &- \frac{ik_s\sqrt{\varepsilon_s}}{2c}M_{yz} - \frac{k_s^2}{6}O_{xzz}^{(e)} - \frac{k_s^2\sqrt{\varepsilon_s}}{6c}O_{yzz}^{(m)}),\end{aligned} \tag{11}$$

Effective polarizabilities can also be used to obtain the transmittance coefficient:

$$\begin{aligned}t =& 1 + \frac{ik_s}{2S_L}(\frac{1}{\varepsilon_0\varepsilon_s}\alpha_p^{\text{eff}} + \alpha_m^{\text{eff}} + \frac{k_0^2}{12\varepsilon_0}\alpha_Q^{\text{eff}} \\ &+ \frac{k_s^2}{4}\alpha_M^{\text{eff}} + \frac{k_s^4}{18\varepsilon_0\varepsilon_s}\alpha_{eo}^{\text{eff}} + \frac{k_s^4}{18}\alpha_{mo}^{\text{eff}}),\end{aligned} \tag{12}$$

where $S_L = D_x D_y$ is the area of a lattice unit cell, and the effective polarizabilities of the ED, MD, EQ, MQ, electric octupole (EOC), and magnetic octupole (MOC) are defined by $\alpha_p^{\text{eff}} = p_x/E_x$, $\alpha_m^{\text{eff}} = m_y/H_y$, $\alpha_Q^{\text{eff}} = 2Q_{xz}/(ik_s E_x)$, $\alpha_M^{\text{eff}} = 2M_{yz}/(ik_s H_y)$, $\alpha_{eo}^{\text{eff}} = -3O_{xzz}^{(e)}/(k_s^2 E_x)$, and $\alpha_{mo}^{\text{eff}} = -3O_{yzz}^{(m)}/(k_s^2 H_y)$, respectively. The normalized effective multipolar polarizabilities are obtained by multiplying by effective polarizabilities with the coefficients in Eq. (12) to compare their relative contribution to transmittance. The transmittance related to the intensity is $T = |t|^2$.

References

[1] D. Haertle, G. Caimi, A. Haldi, G. Montemezzani, P. Günter, A. A. Grabar, I. M. Stoika, and Yu. M. Vysochanskii. Electro-optical properties of $Sn_2P_2S_6$. *Optics Communications*, 215(4):333–343, 2003.

[2] A. Han, J. V. Moloney, and V. E. Babicheva. Applicability of multipole decomposition to plasmonic- and dielectric-lattice resonances. *The Journal of Chemical Physics*, 156(11):114104, 2022.

[3] J. D. Jackson. Classical electrodynamics, 1999.