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Microscopic Interactions Governing Phasematchability in Nonlinear Optical Materials — Electronic Supplementary Information

Antonio Cammarata*a and James Rondinellib

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1 Phase Matching Angles in Biaxial Crystals

Phase matching condition in biaxial crystals is governed by a precise relation¹ involving the refractive index *n* as a function of the frequency ω of the incident light and its value at 2ω , as well as the angles of incidence of the incoming light:

$$\frac{k_x^2}{n_{\omega}^{-2} - n_{x,\omega}^{-2}} + \frac{k_y^2}{n_{\omega}^{-2} - n_{y,\omega}^{-2}} + \frac{k_z^2}{n_{\omega}^{-2} - n_{z,\omega}^{-2}} = 0$$

$$\frac{k_x^2}{n_{z,\omega}^{-2} - n_{z,\omega}^{-2}} + \frac{k_y^2}{n_{z,\omega}^{-2} - n_{y,z,\omega}^{-2}} + \frac{k_z^2}{n_{z,\omega}^{-2} - n_{z,z,\omega}^{-2}} = 0$$
(1)

where $k_x^2 = \sin \theta \cos \phi$, $k_y^2 = \sin \theta \sin \phi$ and $k_z^2 = \cos \theta$; θ is the angle between the wave normals and the *z* axis, ϕ is the angle from the *x* axis in the *xy* plane; $n_{x,\omega}$, $n_{y,\omega}$, $n_{z,\omega}$ and $n_{x,2\omega}$, $n_{y,2\omega}$, $n_{z,2\omega}$ are the three principal refractive indices of the fundamental and the second harmonic waves, respectively; finally, n_{ω} and $n_{2\omega}$ are functions of $n_{i,\omega}$, $n_{i,2\omega}$, k_x , k_y and k_z .

If the components of the refractive index are such to satisfy the condition

$$n_{2\omega} = n_{\omega}, \tag{2}$$

Equation 1 can be resolved for a specific range of θ and ϕ angles and the crystal is said to be of *type I* phase-matchable for the Second Harmonic Generation of the frequency ω . The solutions of Equation 1 are evaluated by fitting the first-principles computed frequency dependent refractive index over the wavelength range [0,4.56] μ m. The numerical results are represented as curves in a (θ , ϕ) diagram, where θ and ϕ are the phase matching angles.

2 Computational Approach

Density functional (perturbation) theory [DF(P)T] calculations within the local-density approximation² (LDA) and the independent electron approximation, neglecting quasi-particle effects, are performed using the ABINIT package³⁻⁶. To achieve high-precision in the relaxed-ion nonlinear dielectric susceptibility, we use a plane-wave cutoff of 800 eV and $5 \times 5 \times 5$ *k*-point mesh. Norm-conserving pseudopotentials, generated with the Troullier-Martins scheme, are used for all atoms with the following valence electron configuration: $2s^1$ (Li), $5s^24d^{10}$ (Cd), $4s^24p^2$ (Ge), $5s^25p^2$ (Sn) and $3s^23p^4$ (S). Unless specified, we use the experimental⁷ atomic positions and crystal structures for all calculations of the Li₂CdGeS₄ (LCG) and Li₂CdSnS₄ (LCS) compounds, respectively.

The second-order dielectric tensor d_{ij} is calculated by means of the DFPT, evaluating the response of the system under electromagnetic perturbations^{8,9}. In nonlinear optical materials, the global response is described in terms of an average *effective* nonlinear coefficient, that is calculated averaging the response along the crystal axes and exploiting the point group symmetries of the system; for the present study, the point group of interest is *mm*2 and the d_{eff} non linear coefficient is defined as

$$d_{eff} = \left[\frac{19}{105}d_{33}^2 + \frac{13}{105}(d_{33}d_{31} + d_{33}d_{32}) + \frac{44}{105}(d_{15}^2 + d_{24}^2) + \frac{13}{105}(d_{15}d_{32} + d_{24}d_{31})\right]^{1/2}.$$
(3)

The complex $\tilde{\epsilon}(\omega) = \epsilon_{\Re}(\omega) + i\epsilon_{\Im}(\omega)$ dielectric function is evaluated by means of the OPTIC utility included in the ABINIT package, using the ground state wavefunction and the wavefunction derivatives with respect to their wavevector. The phase matching condition is expressed in terms of the diagonal components of the refractive index tensor. The *ii* diagonal component of the

^a Department of Control Engineering, Czech Technical University, Technicka 2, 16627 Prague 6, Czech Republic. Fax: +420 224 91 8646; Tel: +420 224 35 7598; E-mail: cammaant@fel.cvut.cz

^b Department of Materials Science & Engineering, Northwestern University, Evanston, IL 60208, USA



Fig. 1 Calculated electronic bandgap as a function of the SAMD for each of the structures in the LCG- and LCS-path. The linear trends justify the use of a constant scissor operator along each path to calculate the properties of the hypothetical systems.

cartesian refractive index $n(\omega)$ tensor is calculated from $\tilde{\varepsilon}(\omega)$ as

$$n_{ii} = \sqrt{\frac{\varepsilon_{\Re,ii} + \sqrt{\varepsilon_{\Re,ii}^2 + \varepsilon_{\Im,ii}^2}}{2}}.$$
(4)

The refractive index and its related properties are very sensitive of the bandgap width at the Fermi level, and qualitative errors are introduced if the bandgap is not properly reproduced. To avoid such artifacts, the scissor operator¹⁰ has been used to shift upwards the conduction band to match the calculated gap with the experimental value. The experimental band gaps have been determined by diffuse-reflectance spectroscopy technique and have been found to be 3.15 and 3.26 eV for LCG and LCS, respectively⁷. Calculations on both Li₂CdGeS₄ and Li₂CdSnS₄ compounds have been based on use of the LDA energy functional that is known to underestimate the band gaps. We find a band gap of 2.54 and 2.39 eV for LCG and LCS, respectively; since these values are lower than the experimental ones, the corresponding valence bands have been shifted up by +0.61 and +0.33 eV, respectively, by applying the scissor operator, in order to match the experimental values. LCS is found to be a direct band gap insulator, while LCG has an indirect band gap, consistent with previous calculations reported in literature¹¹. The calculated nonlinear response is found to be $d_{eff} = 7.03$ and $d_{eff} = 7.66$ pm/V for LCG and LCS, respectively, without the use of the scissor operator; the scissor-corrected values are $d_{eff} = 5.33$ and $d_{eff} = 6.49$ pm/V for LCG and LCS, respectively, corresponding to a relative SHG intensity LCG/LCS=0.7, in agreement with the reported data 12 .

Along the LCG- and LCS-path, the electronic bandgap at the Fermi level increases linearly with the SAMD (Figure 1); such trend suggests that if it were possible to experimentally measure the bandgap of each hypothetical structure along the path, we would observe bandgap values that are shifted by a constant amount with respect to the corresponding calculated values. For this reason, we choose a constant value for the scissor operator to calculate the properties of the hypothetical systems, corresponding to +0.61 and +0.33 eV for the LCG-path and LCS-path, respectively, that coincide with the values used for the LCG and LCS structures.



Fig. 2 Lower limit λ_{min} of the incident wavelengths that satisfy the phasematchability condition as a function of (a) structural distortions, (b) bandgap and (d) covalency of the M–S bond. (c) Covalency of the M-S bond as a function of the structural SAMD.

3 λ_{min} Threshold Dependence on Electro-Structural Features

All the structures of both adiabatic paths satisfy the phasematchability condition for particular values of the λ incident wavelength above a certain thresold λ_{min} . We observe that, at fixed distortion, by changing the M atom it is possible to shift the λ_{min} value [Figure 2(a)]; moreover, λ_{min} has a dependence of the bandgap value that is peculiar of the stoichiometry and does not provide sufficient information on how it is related to the onset of the phasematchability [Figure 2(b)]. To understand the microscopic origin of the onset of the phase matching condition, we need to investigate how the electronic features determine the λ_{min} value. The M atom has the effect to determine the charge distribution along the M–S bond, fixing the $C_{M,S}$ bond covalency at a specific value; on the other hand, $C_{M,S}$ is also determined by the magnitude of the structural distortions [Figure 2(c)]. The SHG response and the minimum wavelength λ_{min} at which the phase matching condition is realized are dictated by the energy level occupancy at the Fermi level edge; for this reason, the $C_{M,S}$ bond covalency determines the λ_{min} value at which the phase matching condition is satisfied [Figure 2(d)]. In both adiabatic paths, we observe that the minimum λ_{min} is realized for the lowest M–S bond covalency value, and λ_{min} globally increases with increasing $C_{M,S}$.

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