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Electronic Supplementary Information

Adjustable Optical Nonlinearity in d^{10} Cations Containing Chalcogenides via *dp* Hybridization Interaction

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Post-processing Tools for the second-harmonic generation (SHG) effect

SHG-density: To our knowledge, SHG-density is a good representation of SHG contribution, with its definition ensures those Kohn-Sharm orbitals making major contribution to SHG process will be shown, however, those Kohn-Sharm orbitals making no contribution to SHG process will not be shown. The SHG-density provides a unbiased way to show SHG distribution in space, and more importantly, to show the connection between active region of SHG process and their participating ions or group of ions. Noting that SHG-Density can visually show the distribution of the strength of SHG, when integrating over space, as can be easily checked from the original formula and definition, it really adds up back to predicted $\chi^{(2)}$.[1]

Band-resolved: From the equations of second-order NLO coefficients, the value of SHG strength can be devided into two representations of orbital contributions, namely occupied and unoccupied bands, based on two different types of summing sequences. Then a plot for the band-resolved SHG coefficient can be calculated, and it clearly shows the orbital contribution of the $\chi^{(2)}$ on a energy or level-by-level basis. By this process, therefore the predominant orbitals giving main contribution to a SHG process will be identified. Since the “band-resolved” plots of SHG coefficient are susceptible to the variation of structure or configuration in a material, through the analysis of the SHG strength from individual orbitals, it can be applied to investigate the detailed mechanism of SHG processes in a material. Besides, re-evaluating $\chi^{(2)}$.using artificially adjusted eigenvalue spectra is beneficial to identify the role played by the energy level of orbitals.[2]

Table S1 The calculated atomic valence orbital energies *s*, *p* and *d* in eV of related elements, band gap, VBM and CBM (eV) by using the local-density approximation within the density functional theory.

Atom	***s*** (eV)	***p*** (eV)	***d*** (eV)	**Compounds**	**Band gap** (eV)	**VBM** (eV)	**CBM** (eV)
Cd	-6.04	-1.41	-11.96	**Li_2CdGeS_4**	2.70	-3.23	-0.53
Hg	-7.21	-1.26	-10.09	**Li_2HgGeS_4**	2.06	-2.93	-0.87

Table S2 The calculated dielectric tensors of for Li_2CdGeS_4 and Li_2HgGeS_4.

Compounds	**Static dielectric permittivity**			**Optical dielectric permittivity**		
	ϵ_{xx}	ϵ_{yy}	ϵ_{zz}	ϵ_{xx}	ϵ_{yy}	ϵ_{zz}
Li_2CdGeS_4	8.13	6.92	7.94	5.06	4.62	4.91
Li_2HgGeS_4	11.45	7.56	9.88	5.84	4.99	5.56

Table S3 The calculated Born effective charges for Li_2CdGeS_4 and Li_2HgGeS_4.

Compounds	**Atoms**	**q_{xx}**	**q_{yy}**	**q_{zz}**	**Nominal charge**	**Δq**	**Birefringence (Δn)**
Li_2CdGeS_4	Li	0.924	1.201	1.069	+1	-0.132	0.02 (@1064)
	Cd	2.380	1.732	2.217	+2	0.485	
	Ge	2.993	2.280	2.880	+4	0.600	
	S1	-2.334	-1.488	-1.539	-2	0.846	
	S2	-1.267	-1.983	-1.857	-2	-0.716	
Li_2HgGeS_4	Li	0.897	1.269	1.091	+1	-0.372	0.05 (@1064)
	Hg	2.774	1.753	2.380	+2	1.021	
	Ge	3.343	2.076	2.985	+4	1.267	
	S1	-2.614	-1.495	-1.566	-2	1.119	
	S2	-1.275	-1.844	-1.972	-2	-0.568	

Notes and references

1 (a) J. Lin, M. H. Lee, Z. P. Liu, C. T. Chen, C. J. Pickard, *Phys. Rev. B*, 1999, **60**, 13380; (b) Z. S. Lin, L, Bai, L, j, Liu, M. H. Lee, J. Xu, X. Y. Wang, C. T. Chen, *J. Appl. Phys.,* 2011, **109**, 073721.

2 M. H. Lee, C. H. Yang, J. H. Jan, *Phys. Rev. B*, 2004, **70**, 235110.