Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Electronic Supplementary Information for:

Metal-Cation Substitutions Induced the Enhancement of Second Harmonic Generation in A_8BS_6 (A = Cu, Ag; B = Si, Ge, Sn)

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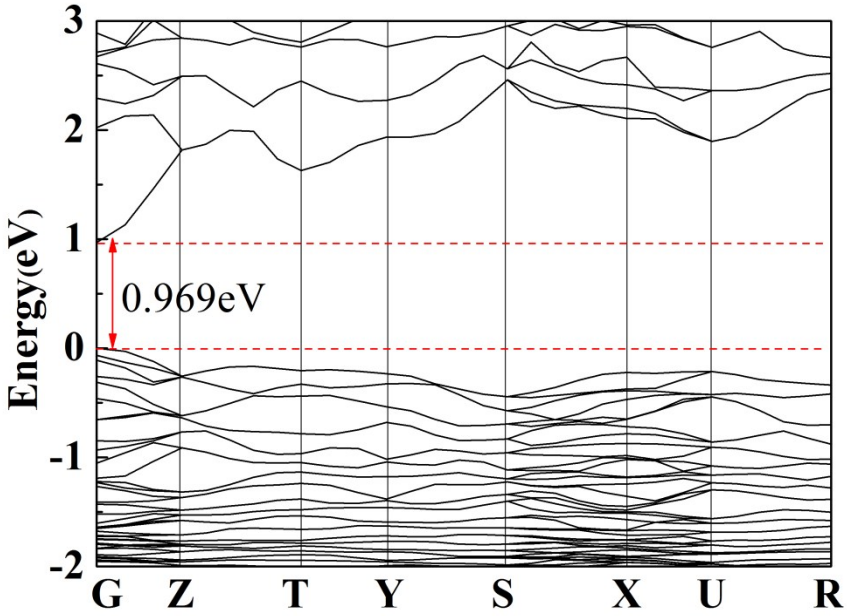
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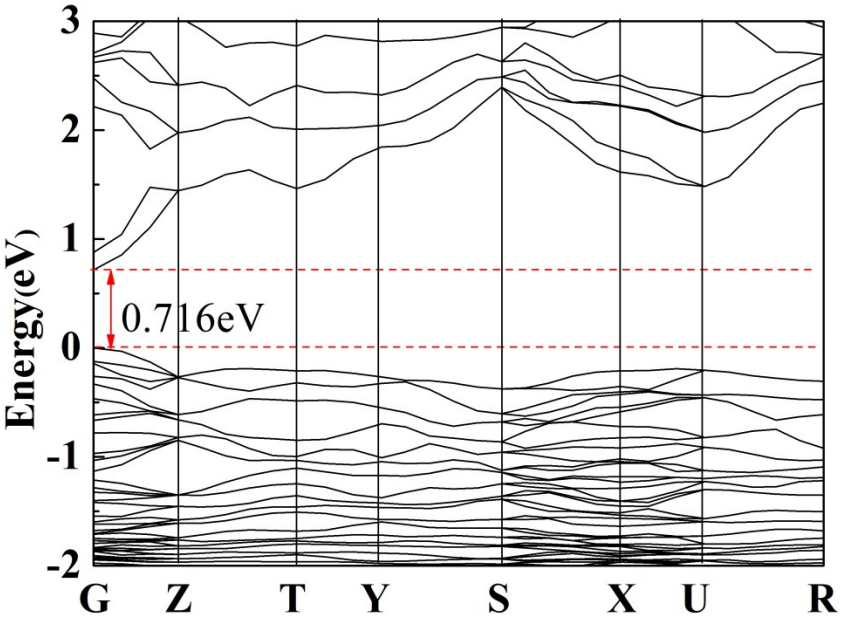
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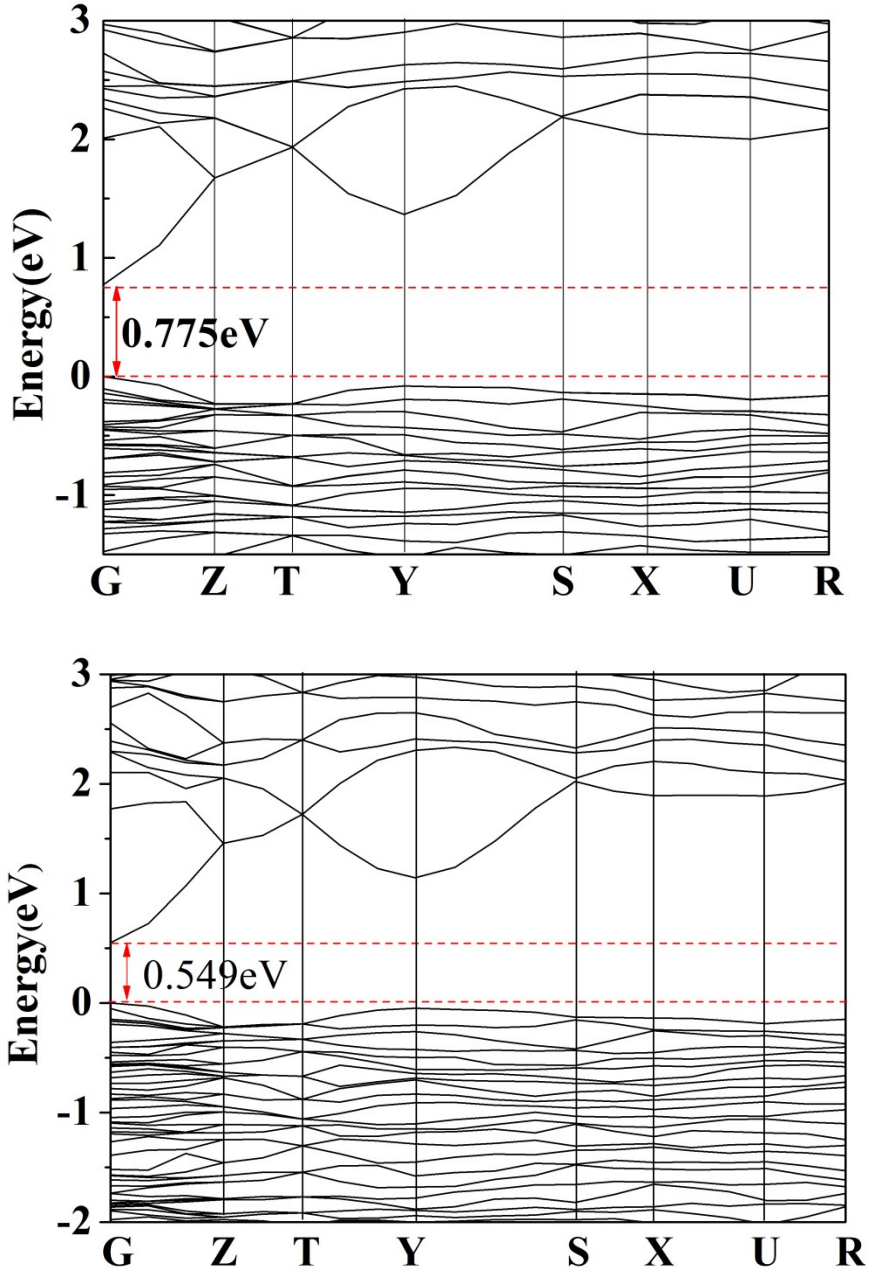


Fig S1 Band structures of Cu_8SiS_6, Cu_8GeS_6, Ag_8GeS_6 and Ag_8SnS_6 calculated along selected high symmetry k-points, Their band structures are qualitatively similar to one another with direct band gap.

Table 1 Crystallographic structural data of compounds Cu_8SiS_6, Cu_8GeS_6, Ag_8GeS_6 and Ag_8SnS_6

	Cu_8SiS_6 [1]	Cu_8GeS_6 [2]	Ag_8GeS_6 [3]	Ag_8SnS_6 [4]
fw	728.45	772.98	1127.51	1,173.59
Space group	$Pmn2_1$	$Pmn2_1$	$Pna2_1$	$Pna2_1$
a (Å)	6.992(2)	7.0445(3)	15.149(1)	15.298(2)
b (Å)	6.901(2)	6.9661(3)	7.476(2)	7.548(2)
c (Å)	9.768(2)	9.8699(5)	10.589(1)	10.699(2)
β(°)	90	90	90	90
V (Å^3)	471.32	484.34	1199.25	1235.41
Z	2	2	4	4
D_{calc} (g·cm^{-3})	5.14	5.30	6.25	6.31
*R*1 (F_o>4σ(F_o))	/	0.087	0.082	/

$R_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$.

Reference

[1] W.F. Kuhs, R Nitsche, Materials Research Bulletin 1979, 14, 241-248.

[2] M. Onoda, X.-A. Chen, K. Kato, H. Wada, Acta Crystallographica, Section B: Structural Science 1999, 55, 721-725.

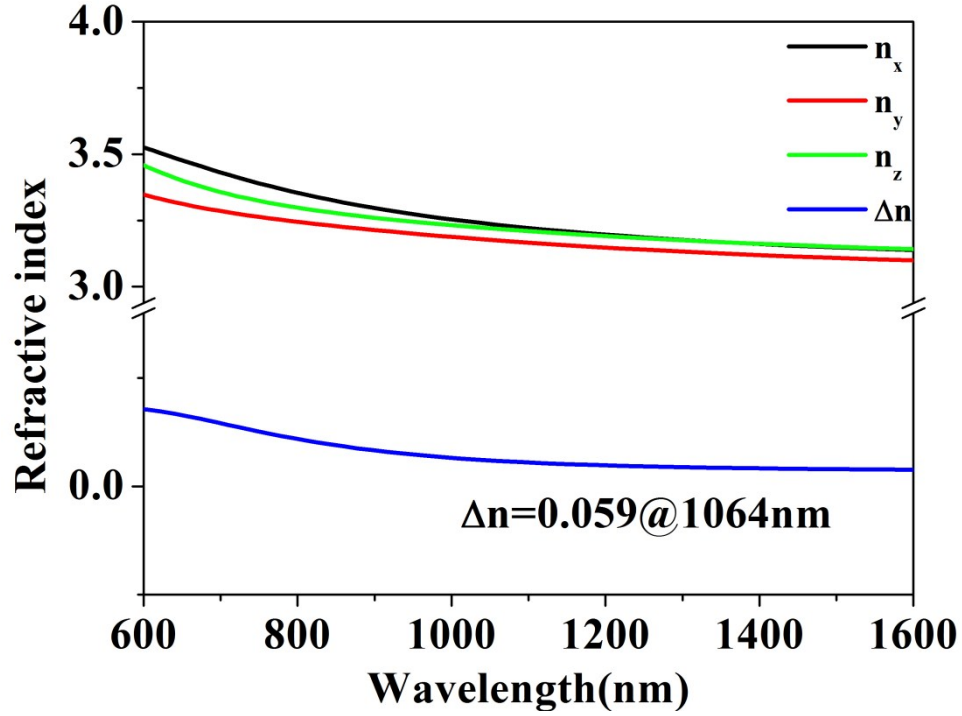
[3] G. Eulenberger, Monatshefte fuer Chemie 1977, 108,901-913.

[4] N, Wang. Neues Jahrbuch fuer Mineralogie, Monatshefte 1978, 1978, 269-272.

Table S2 Local dipolemoment calculation for Cu_8SiS_6, Cu_8GeS_6, Ag_8GeS_6 and Ag_8SnS_6

Compound	species	x(a)	y (b)	z (c)	deby
Cu_8SiS_6	SiS_4	0	0	8.45	10.26
	$Cu(1)S_3$	0	0	-0.04	8.42
	$Cu(3)S_3$	0	0	2.19	12.61
	$Cu(5)S_3$	0	0.86	5.64	6.20
	$Cu(2)S_4$	0	0	-8.21	12.54
	$Cu(4)S_4$	0	0	-6.13	8.02
	$[Cu\ S]_{total}$	0	0.86	1.9	58.05
Cu_8GeS_6	GeS_4	0	-0.94	9.11	9.30

	$Cu(1)S_3$	0	0	-0.15	9.78
	$Cu(3)S_3$	0	0	4.41	12.70
	$Cu(5)S_3$	0	0.40	6.32	6.43
	$Cu(2)S_4$	0	0	-7.55	13.23
	$Cu(4)S_4$	0	1.85	-7.26	9.14
	$[Cu\ S]_{total}$	0	1.31	4.88	60.58
Ag_8GeS_6	GeS_4	0	0	3.31	3.76
	$Ag(8)S_2$	0	0	-4.87	6.06
	$Ag(1)S_3$	0	0	-1.10	1.60
	$Ag(2)S_3$	0	0	-1.65	4.28
	$Ag(6)S_3$	0	0	-0.20	6.64
	$Ag(3)S_4$	0	0	3.95	11.48
	$Ag(4)S_4$	0	0	-6.95	12.77
	$Ag(5)S_4$	0	0	7.53	13.74
	$Ag(7)S_4$	0	0	-5.71	6.51
	$[Ag\ S]_{total}$	0	0	-5.69	66.84
Ag_8SnS_6	SnS_4	0	0	1.41	1.95
	$Ag(8)S_2$	0	0	2.99	3.81
	$Ag(4)S_3$	0	0	10.28	15.43
	$Ag(5)S_3$	0	0	-1.06	6.94
	$Ag(7)S_3$	0	0	2.17	5.90
	$Ag(1)S_4$	0	0	-5.70	12.62
	$Ag(2)S_4$	0	0	5.70	6.66
	$Ag(3)S_4$	0	0	7.24	12.37
	$Ag(6)S_4$	0	0	-3.36	12.06
	$[Ag\ S]_{total}$	0	0	19.67	77.74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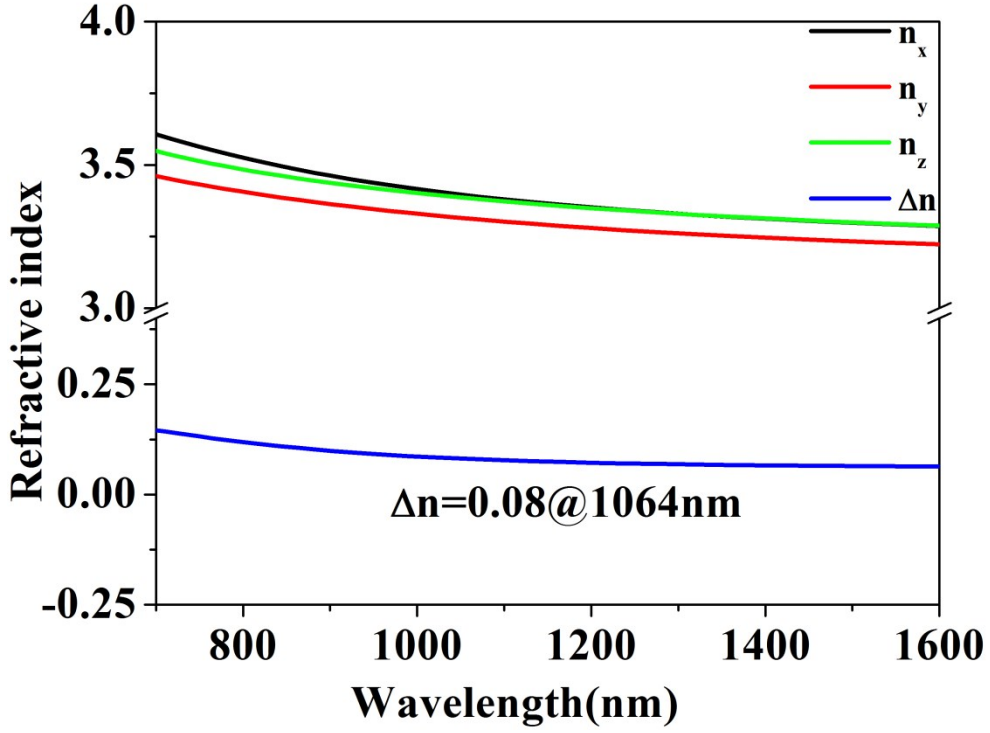
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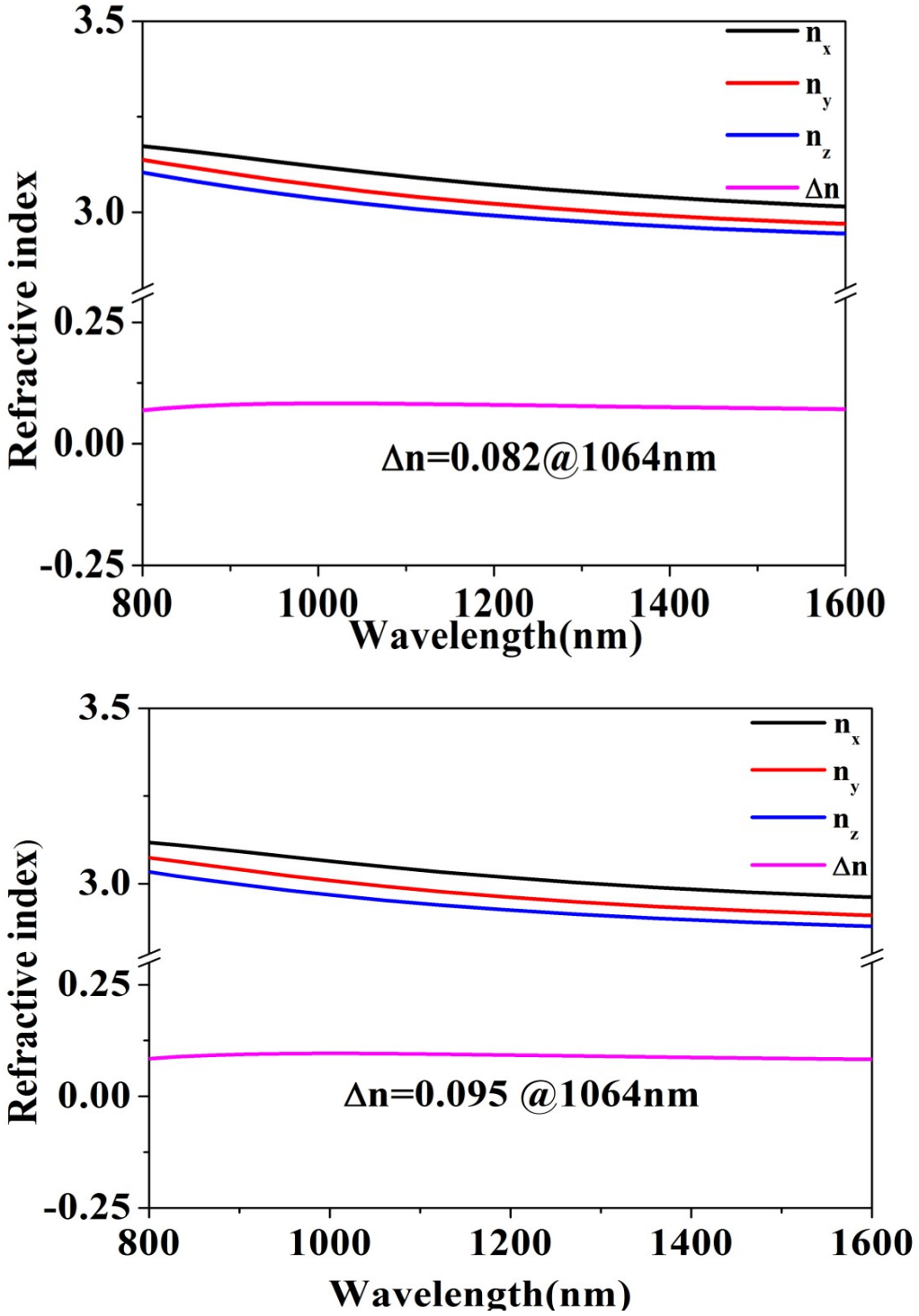

Fig S2 The calculated dispersion curves of birefringence of Cu_8SiS_6, Cu_8GeS_6, Ag_8GeS_6 and Ag_8SnS_6

Table S3 Mulliken population, ionic radii, bond length and volume for Cu_8SiS_6, Cu_8GeS_6, Ag_8GeS_6, Ag_8SnS_6

compound	atom	bond	Bond length	Population	volume(Å^3)	ionic radii

	Cu	Cu-S	2.242-2.648	0.13-0.45		0.73 Å
Cu_8SiS_6	Si	Si-S	2.076-2.158	0.63-0.73	471.52	0.40 Å
	S	/	/	/		
	Cu	Cu-S	2.232-2.598	0.24-0.61		0.73 Å
Cu_8GeS_6	Ge	Ge-S	2.225-2.249	0.44-0.53	484.34	0.53 Å
	S	/	/	/		
	Ag	Ag-S	2.372-2.786	0.17-0.41		1.26 Å
Ag_8GeS_6,	Ge	Ge-S	2.105-2.142	0.54-0.62	1174.46	0.53 Å
	S	/	/	/		
	Ag	Ag-S	2.440-2.797	0.16-0.41		1.26Å
Ag_8SnS_6	Sn	Sn-S	2.221-2.249	0.58-0.66	1235.41	0.69 Å
	S	/	/	/		