

**NaBaM^{III}Q₃ (M^{III} = Al, Ga; Q = S, Se): First quaternary chalcogenides with the
isolated edge-sharing (M^{III}₂Q₆)⁶⁻ dimers**

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Experimental Section

Reagents and Synthesis: All the raw reagents with purities higher than 99.9% were commercially purchased by Aladdin Industrial Inc. and stored in a dry Ar-filled glovebox with controlled oxygen and moisture levels below 0.1 ppm. Since the Na and Ba metals are easily oxidized in air, all the preparation process has been operated in the glovebox. The synthetic procedure of title compounds is as follows: (1) the mixtures of Na, Ba, Al/Ga, and S/Se in the stoichiometric ratio of 1 : 1 : 1 : 3 were loaded into 10 mm inner-diameter silica tubes under Argon atmosphere in a glove box; (2) these tubes were flame-sealed with methane-oxygen flame under a vacuum degree of 10^{-3} Pa; (3) the sealed tubes were placed in a computer-controlled furnace and heating program sett to 850 °C in 30h, and left for 100 h at this temperature to ensure the mixture completely melt, and then slowly cooled to 300 °C at a rate of 3 °C/h, subsequently cooled to room temperature by turning off the furnace. The obtained products were repeatedly washed with N,N-dimethylformamide (DMF) to remove the unreacted reagent. Finally the air stable colorless block-shaped crystals were found.

Single-Crystal X-ray Diffraction (XRD)

Selected flawless single-crystals were used for data collection with a Bruker SMART APEX II 4K CCD diffractometer (Bruker Corporation, Madison, WI, USA) using Mo K α radiation ($\lambda = 0.71073$ Å) at room temperature. The structure was solved by direct methods from the SHELXTL crystallographic software package and refined by full matrix least-squares techniques with final least-squares refinement on F_o^2 with data having $F_o^2 > 2\sigma(F_o^2)$.^[1, 2] Multi-scan method was chosen for absorption correction. Finally, rational anisotropic thermal parameters for all atoms were obtained by the anisotropic refinement and extinction correction. After the crystal structure refined several times the refinement result has converged to the reasonable R values. The subsequent analysis of the element content in the crystal with an energy-dispersive X-ray (EDX) equipped Hitachi S-4800 SEM (Fig S2, Table S3) shows that the molar ratio (Na:Ba: M^{III}:Q) of title compounds are approximately 1:1:1:3. Then the compounds of formula are determined to be NaBaM^{III}Q₃.

Moreover, the final refined structures were also checked with PLATON,^[3] and no other higher symmetry elements were discovered.

Powder X-ray Diffraction (XRD) Measurement.

The powder XRD data were collected on an automated Bruker D2 PHASER X-ray diffractometer equipped with a diffracted monochromator set for Cu Ka ($\lambda = 1.5418 \text{ \AA}$) radiation under the 2θ range from 10° to 70° at the room temperature. As shown in Fig. S1, the experimental XRD patterns are in good agreement with the calculated results derived from the cif data, which demonstrates that the structural model is correct.

UV–vis–Near Infrared (NIR) Diffuse-Reflectance Spectra.

The ground microcrystal powders of title compounds were placed in a pallet for measurement. With Shimadzu SolidSpec-3700DUV spectrophotometer, optical diffuse reflectance spectra were measured in the wavelength range from 190–2600 nm. The reflectance spectrum was converted to absorption using the Kubelka–Munk function for estimating the experimental band gap.

Raman Spectra.

Hand-picked single-crystals were put on an object slide, and then a LABRAM HR Evolution spectrometer equipped with a CCD detector by a 532 nm laser was used to record the Raman spectra. The crystals were simply placed onto a transparent glass slide and a $50\times$ objective lens was used to choose the area of the crystal to be measured. The laser beam had a spot size of 35 μm , its maximum power was set to $\sim 60 \text{ mW}$ and the integration time was set to be 5 s.

Calculation Details.

To further investigate the relationship of structure–property, the electronic structures and optical properties of title compounds were performed by using the highly efficient density functional theory (DFT) method implemented in the CASTEP module.^[4] The generalized gradient approximation (GGA) with Perdew-Burke-Ernzerhof (PBE) function was employed to calculate the electronic band structures and optical properties.^[5]

Brillouin zone involved $2 \times 4 \times 5$ Monkhorst-pack k-point sampling, and Fermi level smearing was taken as 0.05 eV for geometry optimization and other calculations. The following orbital electrons were treated as valence electrons: Na $2s^2 2p^6 3s^1$; Ba $5s^2 5p^6 6s^2$; Ga $3d^{10} 4s^2 4p^1$; Al $3s^2 3p^1$; S $3s^2 3p^4$ and Se $4s^2 4p^4$.

For deeply understanding the cations contributions on the birefringence, the real-space atom-cutting method was performed as following steps, first in order to clearly determine the cutting radius, the Mulliken bond populations were obtained by the CASTEP code. The obtained bond populations of the Ga–S bonds are 0.47–0.79, which indicates that the Ga–S bonds have covalent character. The bond populations of the Na-S and Ba-S bonds are 0.07–0.13 and 0.06–0.15, respectively. The small bond population shows the ionic character of Na-S and Ba-S. According to the above result, the cutting radius of S set as average values of 1.02 Å and 1.84 Å for covalent and ionic bond length, respectively. The cutting radius of Ga atoms was taken as covalent bond length of 1.26 Å, and the ionic bond lengths of Na and Ba were set as 0.95 Å and 1.35 Å, respectively. Finally the obtained birefringence after removal of the Na and Ba atoms were marked as Cut Na, Cut Ba, respectively.

Table S1 Crystal data and structure refinement for NaBaM^{III}Q₃ (M = Ga, Al; Q = S, Se)

Empirical formula	NaBaGaS ₃	NaBaGaSe ₃	NaBaAlS ₃	NaBaAlSe ₃
Formula weight	260.98	339.59	226.79	308.5
Temperature	296(2) K	296(2) K	296(2) K	296(2) K
Wavelength	0.71073 Å	0.71073 Å	0.71073 Å	0.71073 Å
Crystal system	Orthorhombic			
space group	<i>Pnma</i>			
Unit cell dimensions	a = 19.63(2) Å	a = 20.461(13) Å	a = 19.595(2) Å	a = 20.384(6) Å
	b = 8.851(9) Å	b = 9.177(6) Å	b = 8.8375(10) Å	b = 9.171(3) Å
	c = 6.869(7) Å	c = 7.177(4) Å	c = 6.8748(8) Å	c = 7.162(2) Å
Volume	1193(2) Å ³	1347.6(14) Å ³	1190.5(2) Å ³	1338.8(6) Å ³
Calculated density	3.632 g/cm ³	4.603 g/cm ³	3.163 g/cm ³	4.209 g/cm ³
Absorption coefficient	12.044 mm ⁻¹	25.939 mm ⁻¹	7.789 mm ⁻¹	22.303 mm ⁻¹
F(000)	1168	1600	1024	1456
Completeness	98.0%	99.5%	99.9%	99.9%
Goodness-of-fit on F^2	1.033	1.026	1.055	1.029
Final R indices	$R_1 = 0.0286,$	$R_1 = 0.0271,$	$R_1 = 0.0223,$	$R_1 = 0.0232,$
$[F_o^2 > 2\sigma(F_o^2)]^{[a]}$	$wR_2 = 0.0638$	$wR_2 = 0.0447$	$wR_2 = 0.0441$	$wR_2 = 0.0446$
R indices (all data) ^[a]	$R_1 = 0.0390,$	$R_1 = 0.0408,$	$R_1 = 0.0305,$	$R_1 = 0.0315,$
	$wR_2 = 0.0690$	$wR_2 = 0.0487$	$wR_2 = 0.0479$	$wR_2 = 0.0480$
Extinction coefficient	0.0068(2)	0.00047(3)	0.00115(9)	0.00137(6)
Largest diff. peak and hole	0.891 and -1.216 e.A ⁻³	1.174 and -1.296 e.A ⁻³	0.806 and -0.728 e.A ⁻³	0.748 and -1.005 e.A ⁻³

^[a] $R_1 = F_o - F_c / F_o$ and $wR_2 = [w(F_o^2 - F_c^2)^2 / wF_o^4]^{1/2}$ for $F_o^2 > 2\sigma(F_o^2)$

Table S2. Selected bond lengths (Å) and angles (deg) for title compounds

compounds	$M^{III}Q_4$: M-Q (Å)	$M^{III}Q_4$: Q-M-Q (deg)	NaQ_n : Na-Q (Å)	BaQ_7 : Ba-Q (Å)
NaBaGaS₃	Ga1-S: 2.19, 2.42, 2.91×2	S-Ga1-S: 97.6, 105.9, 116.2	Na1-S: 2.71×2, 3.01, 3.10	Ba-S: 3.16, 3.17, 3.2,
	Ga2-S: 2.19, 2.23, 2.37×2	S-Ga2-S: 92.5, 109.6, 121.7	Na2-S: 2.87×2, 2.97, 3.08	3.22, 3.25, 3.26, 3.42
NaBaGaSe₃	Ga1-Se: 2.34, 2.36, 2.42×2	Se-Ga1-Se: 96.7, 106.6, 115.3	Na1-Se: 2.81×2, 3.21, 3.33	Ba-Se: 3.29×2, 3.33,
	Ga2-Se: 2.35, 2.38, 2.48×2	Se-Ga2-Se: 93.6, 109.9, 120.6	Na2-Se: 3.01×2, 3.12, 3.17	3.34, 3.36, 3.38, 3.48
NaBaAlS₃	Al1-S: 2.19, 2.21, 2.26×2	S-Al1-S: 97.2, 105.6, 115.8	Na1-S: 2.72, 3.03, 3.22	Ba-S: 3.10, 3.16, 3.18,
	Al2-S: 2.21, 2.22, 2.32×2	S-Al2-S: 93.5, 109.7, 120.1	Na2-S: 2.88×2, 2.96, 3.11	3.26, 3.27, 3.36
NaBaAlSe₃	Al1-Se: 2.34, 2.44	S-Al1-Se: 94.8, 110.1, 119.1	Na1-Se: 2.80, 3.05, 3.19	Ba-Se: 3.29×2, 3.32,
	Al2-Se: 2.32, 2.33, 2.38×2	S-Al2-Se: 97.8, 105.5, 115.1	Na2-Se: 3.01×2, 3.11, 3.19	3.33, 3.36, 3.38, 3.50

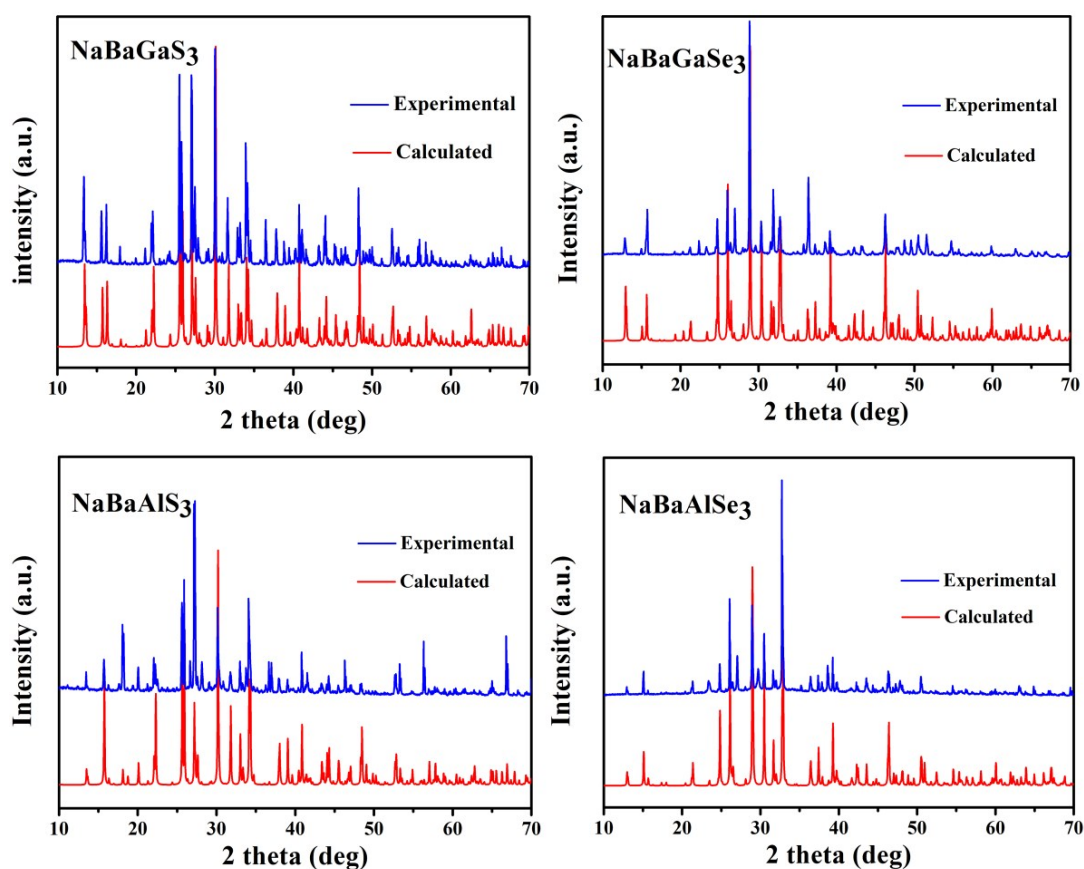


Fig. S1. Powder XRD patterns of title compounds

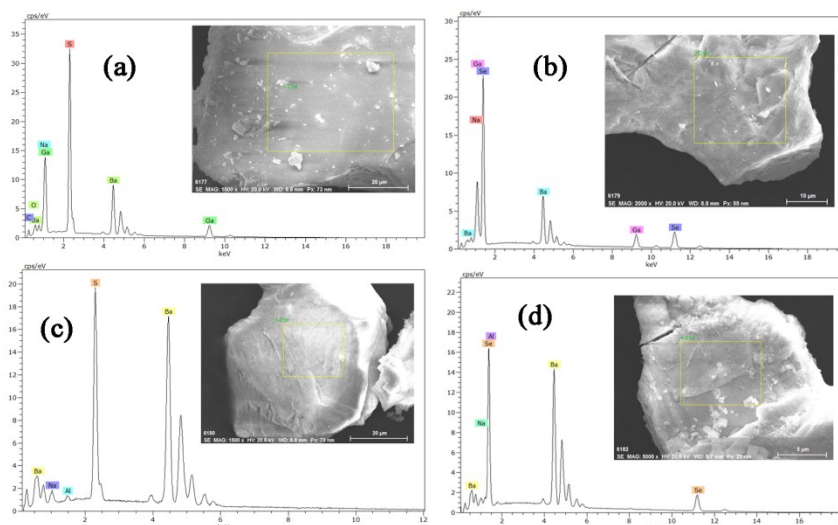


Fig. S2. EDX spectra of title compounds (a) NaBaGaS₃, (b) NaBaGaSe₃, (c) NaBaAlS₃, (d) NaBaAlSe₃.

Table S3. Average EDX data of title compounds

Element	Series	unn. [wt.%]	norm. [wt.%]	Atom. [at.%]	Formula
Ba	L-series	25.94	26.53	15.68	Na _{1.05} Ba _{0.94} Ga _{1.17} S _{2.82}
S	K-series	45.17	45.58	47.04	
Ga	K-series	17.90	18.19	19.66	
Na	K-series	9.37	9.70	17.62	
Ba	L-series	28.08	29.19	16.43	Na _{1.05} Ba _{0.98} Ga _{0.92} Se _{3.03}
Se	K-series	49.70	51.65	50.58	
Ga	K-series	13.41	13.94	15.46	
Na	K-series	5.02	5.21	17.53	
Ba	L-series	27.44	29.25	16.32	Na _{0.81} Ba _{0.97} Al _{0.79} S _{3.41}
S	K-series	48.29	48.72	56.86	
Al	K-series	16.47	16.51	13.27	
Na	K-series	5.51	5.52	13.55	
Ba	L-series	25.44	27.18	15.93	Na _{0.94} Ba _{0.96} Al _{0.96} Se _{3.15}
Se	K-series	47.04	49.84	52.50	
Al	K-series	16.57	16.65	15.95	
Na	K-series	6.26	6.33	15.62	
Total:			100	100	

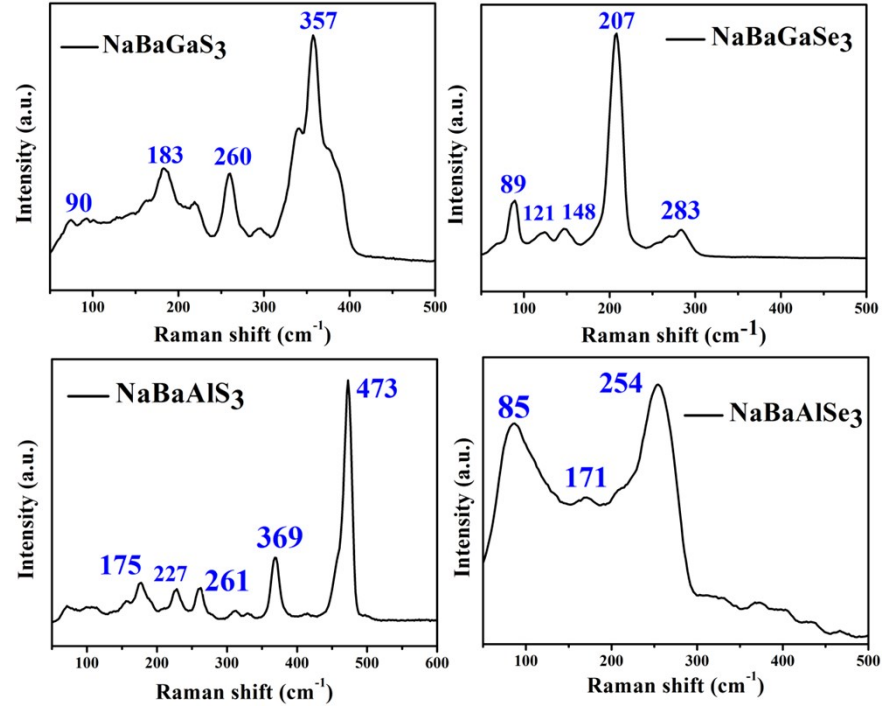


Fig. S3. Raman spectra of title compounds.

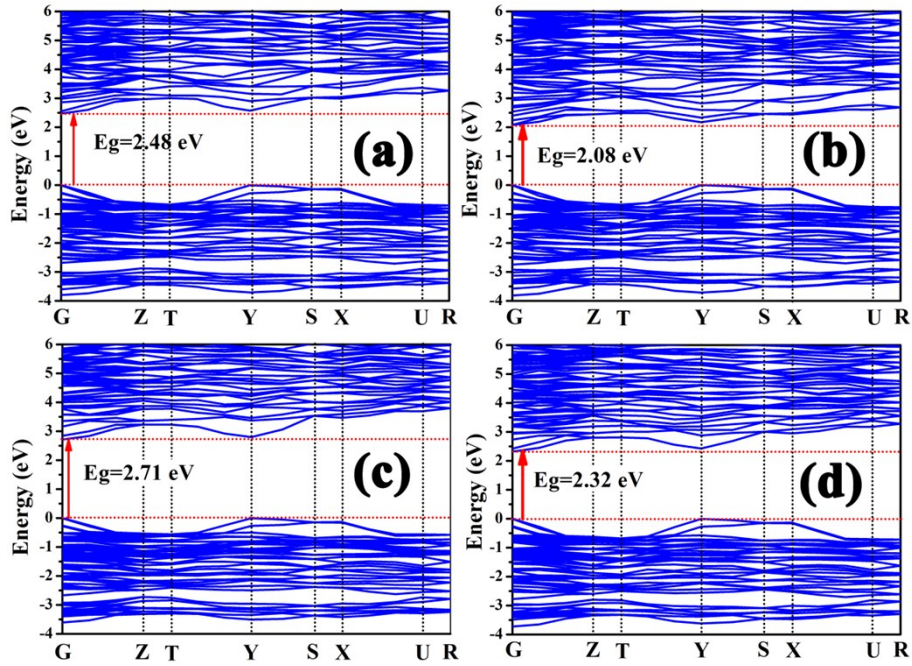


Fig. S4. Calculated band structures of title compounds: (a) NaBaGaS₃, (b) NaBaGaSe₃, (c) NaBaAlS₃, (d) NaBaAlSe₃.

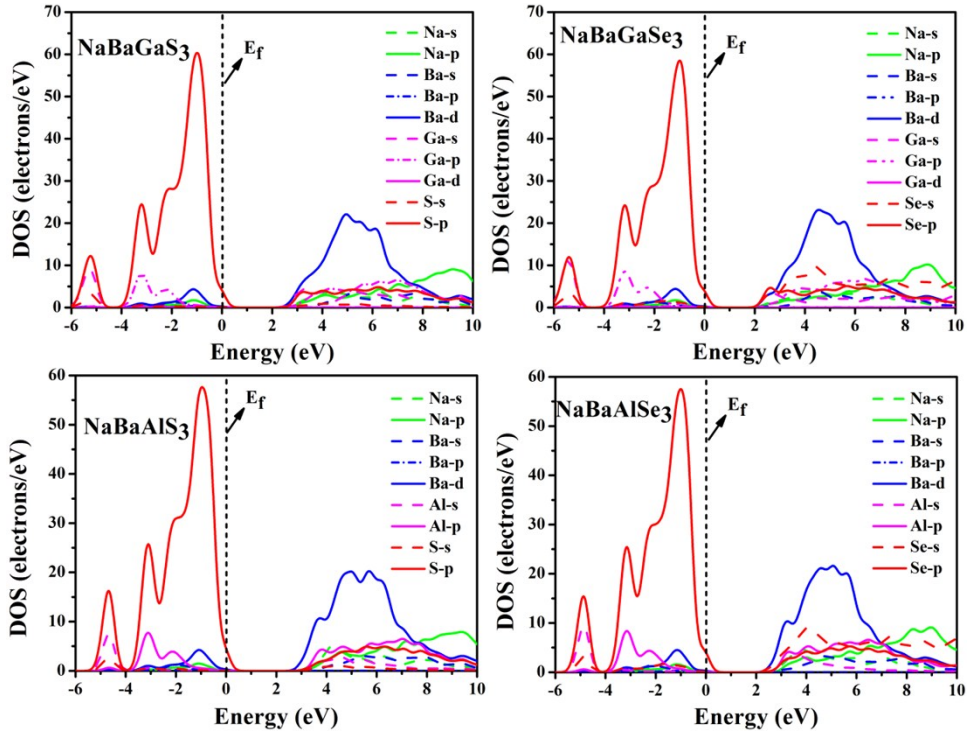


Fig. S5. Partial densities of states of title compounds.

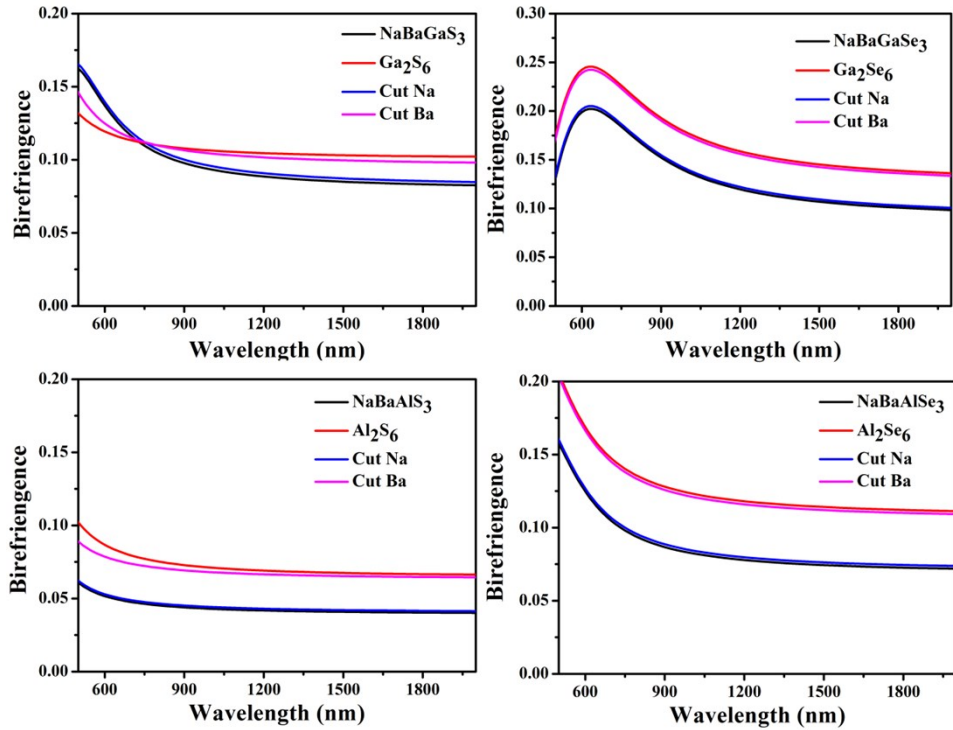


Fig. S6. The contribution of different groups on birefringence

Table S4. Birefringence of different group for title compounds

Different groups	Birefringence (1064 nm)	Birefringence (532 nm)
NaBaGaS₃	0.091	0.155
Ga ₂ S ₆	0.105	0.128
Cut Na	0.093	0.156
Cut Ba	0.103	0.137
NaBaAlS₃	0.042	0.056
Al ₂ S ₆	0.071	0.092
Cut Na	0.044	0.058
Cut Ba	0.067	0.084
NaBaGaSe₃	0.123	0.164
Ga ₂ Se ₆	0.168	0.208
Cut Na	0.131	0.167
Cut Ba	0.165	0.204
NaBaAlSe₃	0.081	0.145
Al ₂ S ₆	0.120	0.191
Cut Na	0.082	0.147
Cut Ba	0.119	0.188

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