Supporting Information

Design and synthesis of a nonlinear optical material $BaAl_4S_7$ with a wide band gap inspired from SrB_4O_7

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Contents

Experimental and calculation details.

Electronic structure calculations

The calculated band structure of $BaAl_4S_7$ is shown in Figure S1. $BaAl_4S_7$ has an indirect bandgap of 3.9 eV at the Γ point, which is less than the experimental value. However, it is larger than that of the existed calculation results, which reported it possessed a band gap with 3.74 eV[1] using the HSE06 method. Figure S1 (b) displays the density of states (DOS) and partial (PDOS) of the respective species in $BaAl_4S_7$. Clearly, the deep part of VB lower than -20 eV is mainly composed of Ba 6s orbitals. The upper part of the VB (-15 to -10 eV) consists of Ba 5p, Al 3p and S 3s orbitals. The VB maximum is exclusively occupied by S 2p and Al 3p orbitals, which is similar to the $BaAl_4Se_7$. The bottom of the CB is mainly contributed from Al 3s, 3p and S 3p orbitals.

In comparison with that of the existed PDOS figure using with GGA-PBE method, it stated that the band gap is found between S-3p orbital VB and Al-3p, Al-3s orbitals CB, which is different from the above calculation result. Since the optical effects of a crystal are mainly determined by the optical transition between the electronic states close to the bandgap, it is anticipated that they are dominantly contributed from the groups constructed by Al and S, while the contribution from the orbitals of the Ba^{2+} cations is negligibly small.

Figure S1. The single crystals of $BaAl_4S_7$.

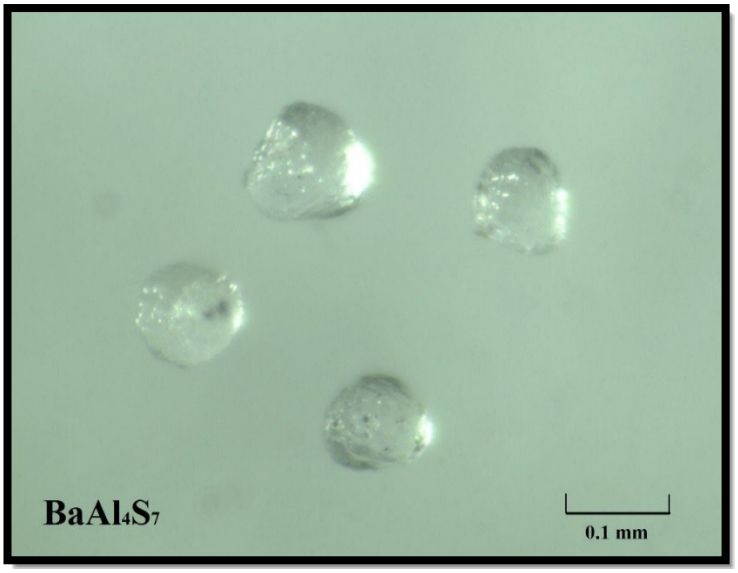

Figure S2. a) Band structure of $BaAl_4S_7$, b) PDOS of $BaAl_4S_7$

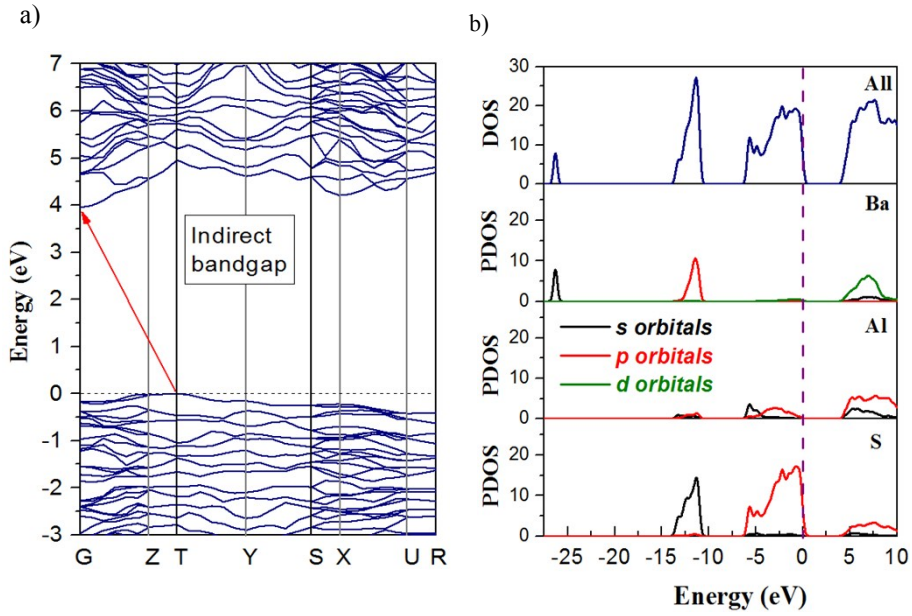

Figure S3. Diffuse spectrum of $BaGa_4S_7$ and $LiGaS_2$: (a, b) the spectrum with upper tangent; (c, d) the spectrum with baseline tangent.

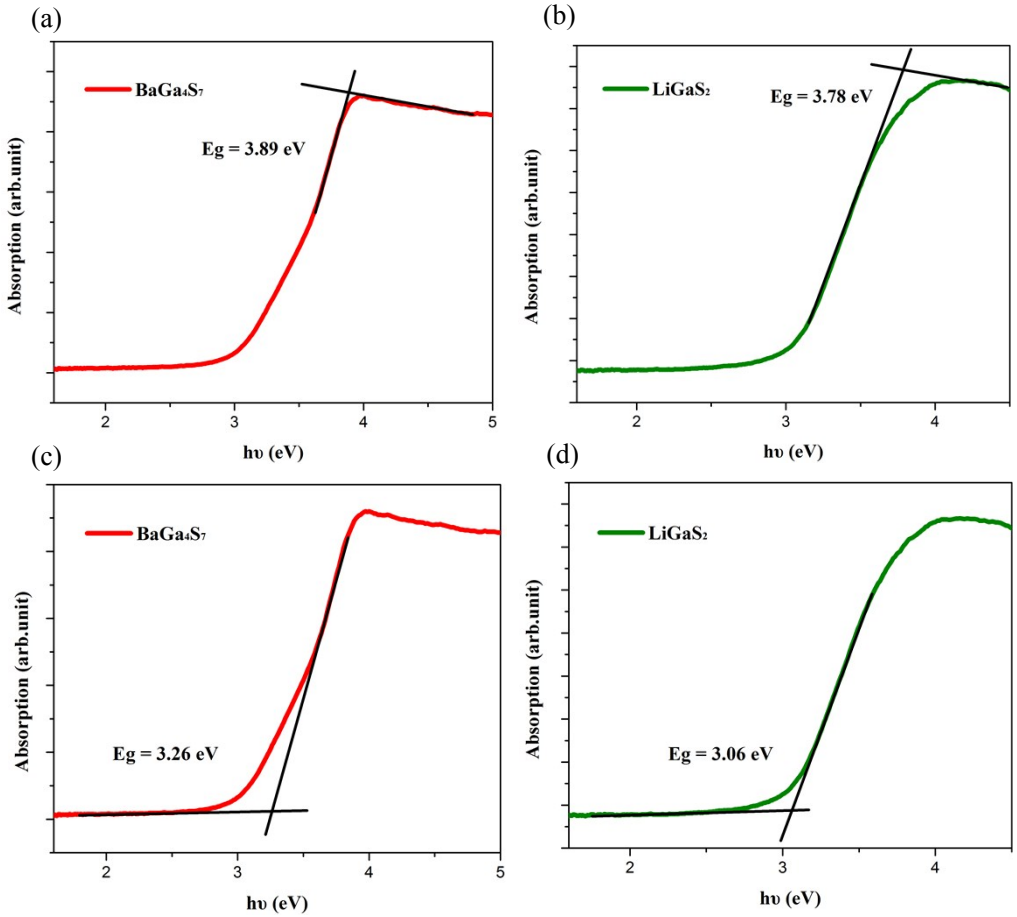

Figure S4. The SHG intensity of a $BaAl_4S_7$ sample compared with that of $AgGaS_2$ at 1.06 μm laser.

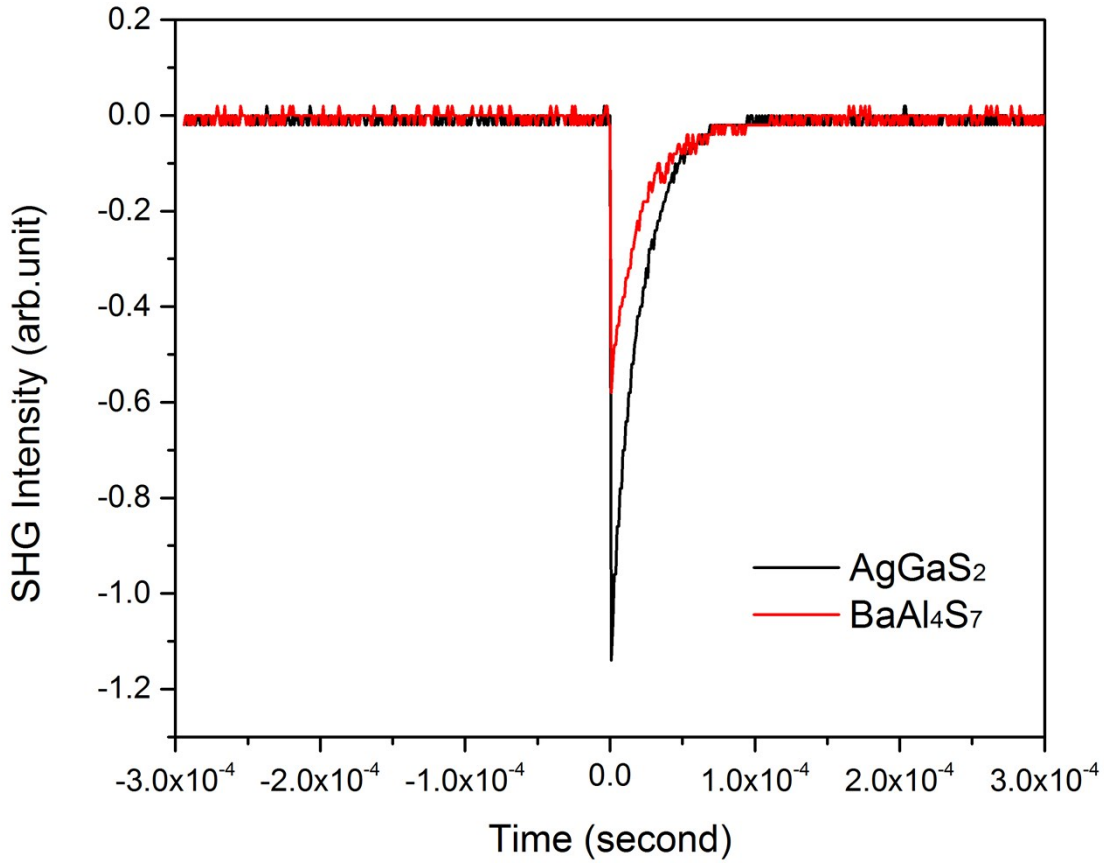

Table S1：Crystal Data and Structure Refinement for $BaAl_4S_7$

	$BaAl_4S_7$
a (Å)	14.748
b (Å)	6.204
c (Å)	5.869
V (Å^3)	537.0
Space group	*$Pmn2_1$ (31)*
Z	2
Index ranges	-19≤h≤19
	-6≤k≤7
	-8≤l≤6
theta range	3.563-28.976
ρ_c(g/cm^3)	2.905
μ(cm^{-1})	53.22
$R(F)^a$	0.04
$R_w(F_o^2)^b$	0.0925

Table S2： Selected Bond Lengths (Å) for $BaAl_4S_7$

Atoms	Distances	Atoms	Distances
Al1-S1	2.201(3)	Ba1-S4	3.398(5)
Al1-S2	2.205(3)	Ba1-S1×2	3.4202(19)
Al1-S3	2.293(3)	Ba1-S2×2	3.490(5)
Al1-S3	2.300(5)	Ba1-S4	3.583(6)
Al2-S4	2.218(3)	Ba1-S2×2	3.592(5)
Al2-S2	2.222(3)	Ba1-S3×2	3.6803(15)
Al2-S1	2.234(5)	Ba1-S1×2	3.6977(18)
Al2-S3	2.301(3)		

REFERENCES

1. A. Benghia, T. Dahame and B. Bentria, *Opt. Mater.*, 2016, **54**, 269-275.