Electronic Supplementary Information

Li_3AlSiO_5: The First Aluminosilicate as a Potential Deep-Ultraviolet Nonlinear Optical Crystal with the Quaternary Diamond-like Structure

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Table S1. Atomic coordinates ($\times 10^4$), equivalent isotropic displacement parameters ($Å^2 \times 10^3$) and bond valence sums (BVS) for Li_3AlSiO_5. *U*(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Atoms	Wyck.	*x*	*y*	*z*	*U*(eq)	BVS
Al(1)	4*a*	3284(1)	7998(1)	3979(3)	7(1)	2.75
Li(1)	4*a*	-3280(7)	8031(3)	8970(30)	13(1)	0.97
Li(2)	4*a*	6650(6)	9960(2)	8940(30)	9(1)	1.01
Li(3)	4*a*	1702(7)	956(3)	8960(20)	14(1)	0.93
Si(1)	4*a*	1668(1)	9015(1)	8945(2)	6(1)	3.93
O(1)	4*a*	3120(3)	9864(1)	7990(3)	9(1)	1.91
O(2)	4*a*	-1217(4)	8979(1)	8034(4)	10(1)	1.91
O(3)	4*a*	3109(3)	8146(1)	7656(3)	10(1)	2.00
O(4)	4*a*	1924(4)	8904(1)	2384(4)	9(1)	2.04
O(5)	4*a*	1454(3)	7102(1)	3097(3)	9(1)	1.94

Table S2. Selected bond lengths (Å) and angles (◦)for Li_3AlSiO_5.

Al(1)-O(5)#1	1.749(2)	O(4)#2-Al(1)-O(3)	107.72(10)
Al(1)-O(5)	1.7533(19)	O(2)-Li(1)-O(5)#9	110.9(5)
Al(1)-O(4)#2	1.759(2)	O(2)-Li(1)-O(3)#10	114.1(4)
Al(1)-O(3)	1.776(3)	O(5)#9-Li(1)-O(3)#10	104.4(4)
Li(1)-O(2)	1.892(5)	O(2)-Li(1)-O(3)#11	114.1(4)
Li(1)-O(5)#9	1.990(14)	O(5)#9-Li(1)-O(3)#11	103.6(4)
Li(1)-O(3)#10	2.033(6)	O(3)#10-Li(1)-O(3)#11	108.8(4)
Li(1)-O(3)#11	2.072(6)	O(1)-Li(2)-O(2)#4	116.9(3)
Li(2)-O(1)	1.942(5)	O(1)-Li(2)-O(1)#14	107.6(5)
Li(2)-O(2)#4	1.952(5)	O(2)#4-Li(2)-O(1)#14	107.0(4)
Li(2)-O(1)#14	1.959(14)	O(1)-Li(2)-O(4)#7	109.8(4)
Li(2)-O(4)#7	2.062(7)	O(2)#4-Li(2)-O(4)#7	112.0(4)
Li(3)-O(1)	1.916(5)	O(1)#14-Li(2)-O(4)#7	102.4(4)
Li(3)-O(2)#12	1.969(11)	O(1)-Li(3)-O(2)#12	109.7(4)
Li(3)-O(5)#15	2.075(5)	O(1)-Li(3)-O(5)#15	121.8(3)
Li(3)-O(4)#6	2.086(6)	O(2)#12-Li(3)-O(5)#15	102.4(3)
Si(1)-O(1)	1.597(2)	O(1)-Li(3)-O(4)#6	111.8(3)
Si(1)-O(2)	1.599(2)	O(2)#12-Li(3)-O(4)#6	103.3(3)
Si(1)-O(4)	1.659(2)	O(5)#15-Li(3)-O(4)#6	106.2(3)
Si(1)-O(3)	1.672(2)	O(1)-Si(1)-O(2)	114.70(9)
O(5)#1-Al(1)-O(5)	114.14(8)	O(1)-Si(1)-O(4)	109.22(10)
O(5)#1-Al(1)-O(4)#2	111.39(10)	O(2)-Si(1)-O(4)	110.20(11)
O(5)-Al(1)-O(4)#2	107.69(11)	O(1)-Si(1)-O(3)	109.89(11)
O(5)#1-Al(1)-O(3)	107.52(10)	O(2)-Si(1)-O(3)	108.21(10)
O(5)-Al(1)-O(3)	108.18(10)	O(4)-Si(1)-O(3)	104.08(9)

Symmetry transformations used to generate equivalent atoms:

#1 x+1/2,-y+3/2,z	#2 x,y,z-1	#3 x+1/2,-y+3/2,z-1
#4 x+1,y,z	#5 x+1,y,z-1	#6 -x,-y+2,z-1/2
#7 -x+1,-y+2,z-1/2	#8 -x+1/2,y-1/2,z-1/2	#9 x-1/2,-y+3/2,z+1
#10 x-1,y,z	#11 x-1/2,-y+3/2,z	#12 -x,-y+2,z+1/2
#13 x-1,y,z+1	#14 -x+1,-y+2,z+1/2	#15 -x+1/2,y+1/2,z+1/2
#16 x,y,z+1		

Table S3 State energies (eV) of the lowest conduction band (L-CB) and the highest valence band (H-VB) at same k-points of Li_3AlSiO_5 calculated by LDA **(a)** and PBE0 **(b)**, respectively.

(a)

Compound	K-piont	H-VB(eV)	L-CB(eV)
Li_3AlSiO_5	G (0.000, 0.000, 0.000)	-0.10141	6.05443
	Z (0.000,0.000, 0.500)	-0.01463	7.85416
	T (-0.500, 0.000, 0.500)	-0.23281	7.99235
	Y (-0.500, 0.000, 0.000)	-0.00719	7.63515
	S (-0.500,0.500, 0.000)	-0.01032	7.70946
	X (0.000,0.500, 0.000)	-0.11899	6.31007
	U (0.000,0.500, 0.500)	0	7.8581
	R (-0.500,0.500, 0.500)	-0.23322	7.98436

(b)

Compound	K-piont	H-VB(eV)	L-CB(eV)
Li_3AlSiO_5	G (0.000, 0.000, 0.000)	-0.20482	7.28592
	Z (0.000,0.000, 0.500)	-0.00524	9.0722
	T (-0.500, 0.000, 0.500)	-0.23281	9.8446
	Y (-0.500, 0.000, 0.000)	-0.0521	7.63515
	S (-0.500,0.500, 0.000)	-0.05351	9.04194
	X (0.000,0.500, 0.000)	-0.19958	7.52171
	U (0.000,0.500, 0.500)	0	9.07362
	R (-0.500,0.500, 0.500)	-0.20842	9.84183

Fig.S1 (a) Optical images of Li_3AlSiO_5 by spontaneous crystallization; **(b)** Observed theoretical morphology of Li_3AlSiO_5.

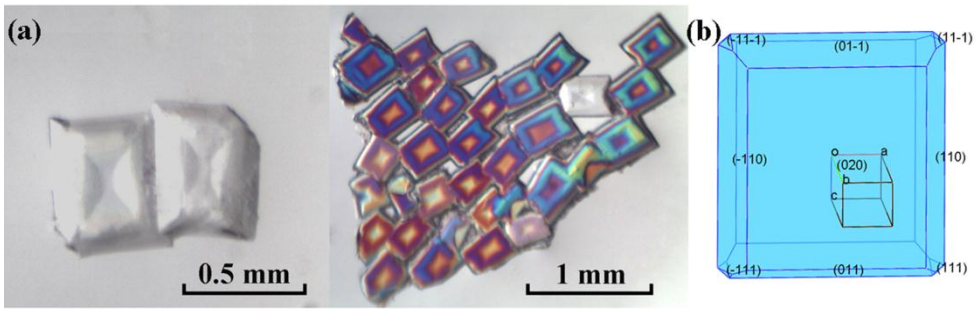


Fig. S2 Thermal ellipsoid plot (50% probability) of the asymmetric unit of Li_3AlSiO_5.

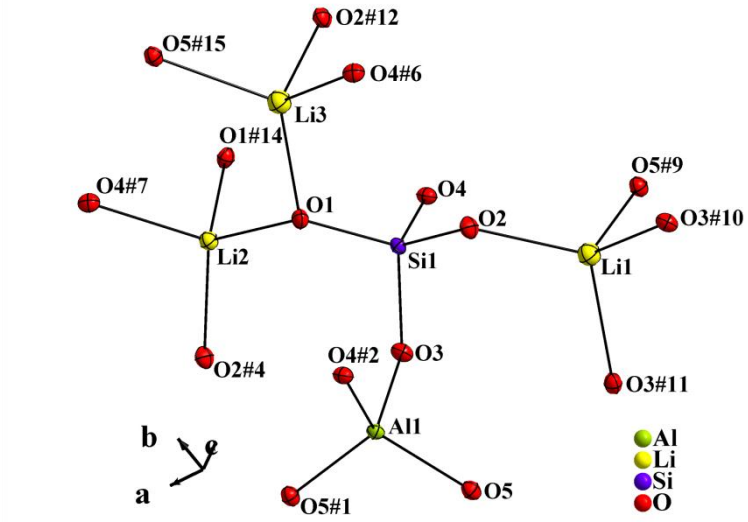


Fig. S3 The arrangement of $[AlSiO_5]^{3-}$slabs view along the a-axis **(a)** and the c-axis **(b)**.(The green tetrahedra represent AlO_4; the purple tetrahedra represent SiO_4)

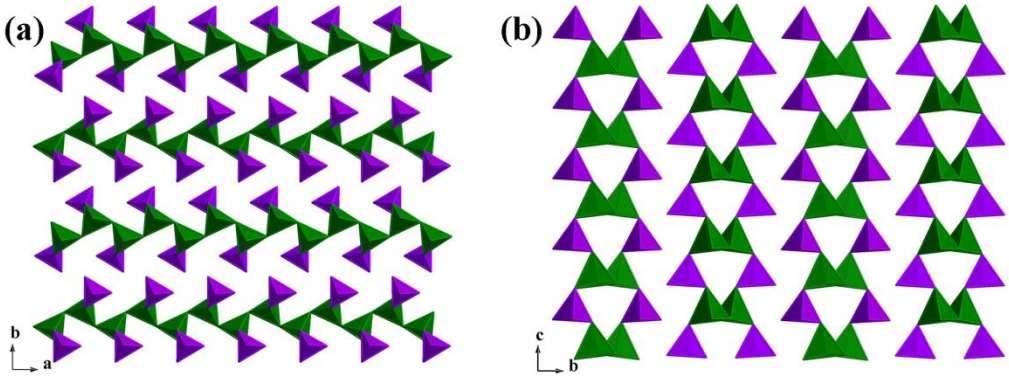


Fig. S4 IR spectrum of Li_3AlSiO_5.

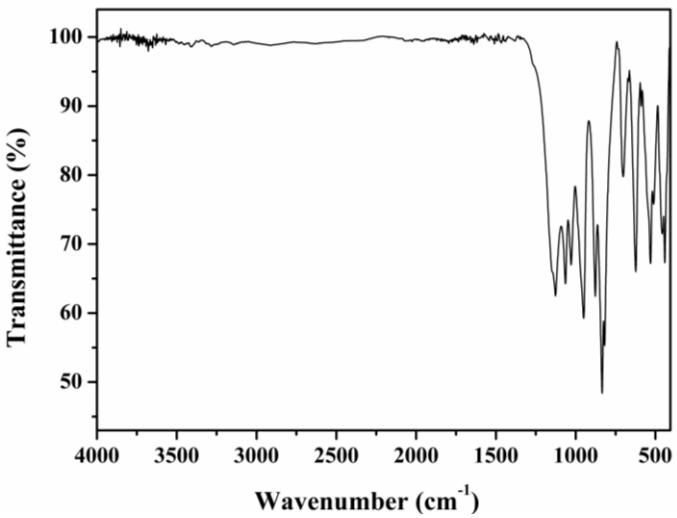


Fig. S5 UV-Vis-NIR diffuse reflectance spectrum of Li_3AlSiO_5.

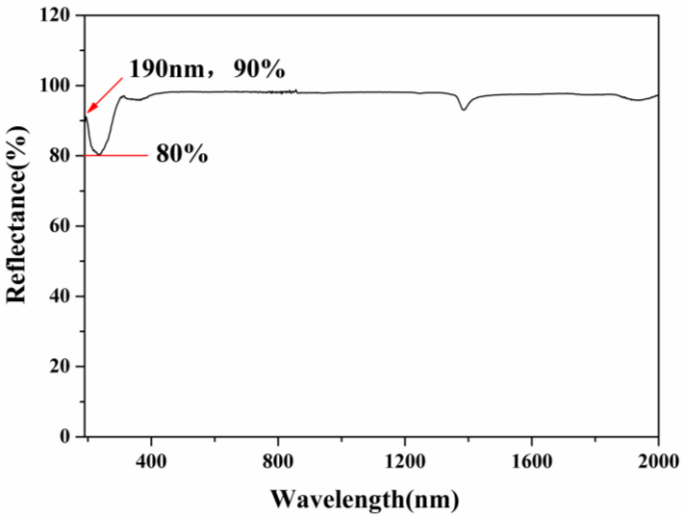


Fig. S6 TG and DSC curves of Li_3AlSiO_5.

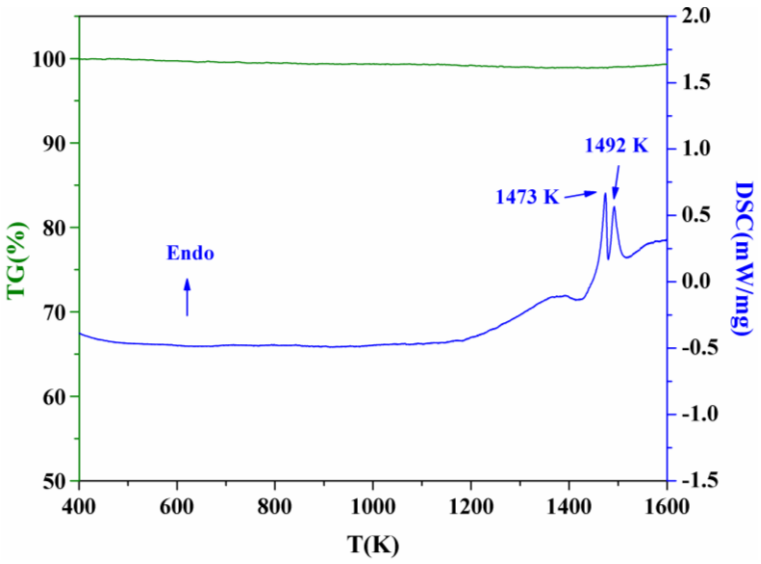
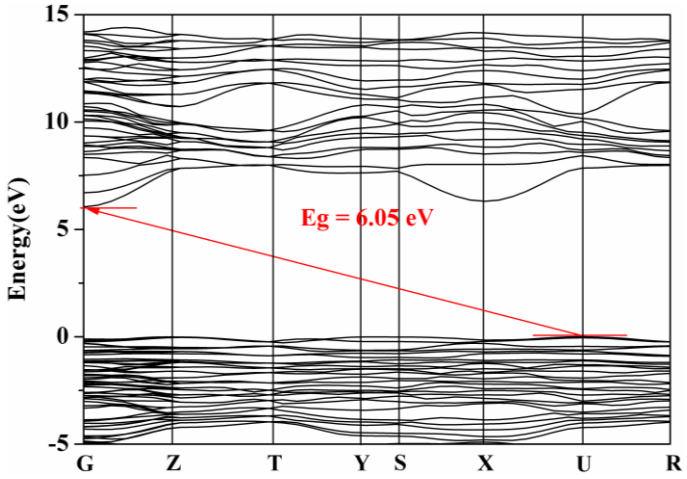


Fig. S7 Calculated band structure of Li_3AlSiO_5 by DFT **(a)** and PBE0 **(b)**.

(a)



(b)