materials

MDPI

Supporting Information

Syntheses, Structures and Properties of Alkali and Alkaline Earth Metal Diamond-like Compounds Li_2MgMSe_4 (M = Ge, Sn)

Hongbo Gao [1,2,†], Kewang Zhang [1,3,†], Ailijiang Abudurusuli [1,4], Chen Bai [1], Zhihua Yang [1], Kangrong Lai [2], Junjie Li [1,*] and Shilie Pan [1,*]

[1] CAS Key Laboratory of Functional Materials and Devices for Special Environments, Xinjiang Technical Institute of Physics & Chemistry, CAS; Xinjiang Key Laboratory of Electronic Information Materials and Devices, 40-1 South Beijing Road, Urumqi 830011, China; hbgao21@gia.cas.cn (H.G.); zhangkewang@stu.xju.edu.cn (K.Z.); ailijiang18@mails.ucas.ac.cn (A.A.); baichen20@ms.xjb.ac.cn (C.B.); zhyang@ms.xjb.ac.cn (Z.Y.)

[2] Department of Physics, Changji University, Changji 831100, China; laikr0212@cjc.edu.cn

[3] College of Physical Science and Technology, Xinjiang University, Urumqi 830046, China

[4] Center of Materials Science and Optoelectronics Engineering, University of Chinese Academy of Sciences, Beijing 100049, China

* Correspondence: lijunjie@ms.xjb.ac.cn (J.L.); slpan@ms.xjb.ac.cn (S.P.)

† These authors contributed equally.

* The calculated details for the contribution of each PDOS on the band gaps in $Li_2MgSnSe_4$, $Li_2MgGeSe_4$.

The contribution of each PDOS on the band gaps was calculated from the following formula:

$$\%_{contribution} = \frac{S_{PDOS}}{S_{TDOS}} \quad \text{(S1)}$$

Here, *%contribution* is the contribution of each PDOS, S_{PDOS}/S_{TDOS} is the integral of each PDOS/TDOS at near the Fermi level.

Table S1. Atomic coordinates and equivalent isotropic displacement parameters of $Li_2MgSnSe_4$. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Atom	x	y	z	U(eq)
Sn(1)	0	3280.6 (13)	9172 (15)	15.6 (3)
Mg(1)	2440 (6)	8297 (9)	9320 (50)	17 (4)
Li(1)	2440 (6)	8297 (9)	9320 (50)	17 (4)
Li(2)	0	6540 (30)	4000 (200)	16 (14)
Se(1)	0	6574 (2)	7943 (3)	19.1 (4)
Se(2)	0	3211 (2)	12929 (3)	18.5 (5)
Se(3)	2467.9 (13)	1665.7 (16)	7982.1 (19)	18.4 (4)

Table S2. Anisotropic displacement parameters ($Å^2×10^3$) of $Li_2MgSnSe_4$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Sn(1)	17.8 (5)	17.1 (5)	11.9 (7)	0.5 (8)	0	0
Mg(1)	24 (4)	22 (4)	6 (11)	3 (5)	4 (5)	-3 (2)
Li(1)	24 (4)	22 (4)	6 (11)	3 (5)	4 (5)	-3 (2)
Li(2)	27 (13)	13 (12)	10 (40)	0 (20)	0	0
Se(1)	20.6 (8)	17.9 (8)	18.6 (11)	3.6 (13)	0	0
Se(2)	18.0 (8)	23.5 (8)	14.1 (12)	2.5 (18)	0	0
Se(3)	19.8 (6)	21.1 (6)	14.5 (10)	-0.8 (10)	3.1 (6)	2.0 (4)

Table S3. Symmetry, selected bond lengths and angles of crystal data and structural refinements of $Li_2MgSnSe_4$.

Sn(1)-Se(1)	2.505 (5)	**Se(1)-Sn(1)-Se(2)**	110.4 (3)
Sn(1)-Se(2)	2.528 (11)	**Se(1)-Sn(1)-Se(3)**	109.3 (2)
Sn(1)-Se(3)#1	2.507 (4)	**Se(1)-Sn(1)-Se(3)#1**	109.3 (2)
Sn(1)-Se(3)	2.507 (4)	**Se(3)-Sn(1)-Se(2)**	108.1 (2)
Li(1)-Se(1)	2.567 (14)	**Se(3)#1-Sn(1)-Se(2)**	108.1 (2)
Li(1)-Se(2)#2	2.583 (13)	**Se(3)#1-Sn(1)-Se(3)**	111.6 (3)
Li(1)-Se(3)#3	2.47 (3)	**Se(1)-Li(1)-Se(2)#2**	109.4 (8)
Li(1)-Se(3)#4	2.581 (14)	**Se(1)-Li(1)-Se(3)#3**	109.5 (8)
Li(2)-Se(1)	2.65 (16)	**Se(3)#4-Li(1)-Se(1)**	113.0 (7)
Li(2)-Se(2)#5	2.50 (4)	**Se(3)#3-Li(1)-Se(2)#2**	105.0 (7)
Li(2)-Se(3)#2	2.58 (5)	**Se(3)#4-Li(1)-Se(2)#2**	109.9 (7)
Li(2)-Se(3)#6	2.58 (5)	**Se(3)#4-Li(1)-Se(3)#3**	109.7 (7)
		Se(2)#5-Li(2)-Se(1)	107 (4)
		Se(2)#5-Li(2)-Se(3)#2	114 (3)
		Se(2)#5-Li(2)-Se(3)#6	114 (3)
		Se(3)#2-Li(2)-Se(1)	105 (3)
		Se(3)#6-Li(2)-Se(1)	105 (3)
		Se(3)#2-Li(2)-Se(3)#6	111 (3)

#1 −x,+y,+z #2 1/2 − x,1 − y,−1/2 + z #3 +x,1 + y,+z #4 1/2 − x,1 − y,1/2 + z.
#5 +x,+y,−1 + z #6 −1/2 + x,1 − y,−1/2 + z #7 −1/2 + x,1 − y,1/2 + z.
#8 +x,+y,1 + z #9 +x,−1 + y,+z.

Table S4. Atomic coordinates and equivalent isotropic displacement parameters of $Li_2MgGeSe_4$. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Atom	x	y	z	U(eq)
Ge(1)	10000	1762.4 (8)	6416.9 (9)	6.43 (11)
Mg(1)	7419 (3)	3215 (4)	1428 (6)	10.5 (4)
Li(1)	7419 (3)	3215 (4)	1428 (6)	10.5 (4)
Li(2)	5000	1560 (20)	6570 (30)	21 (3)
Se(1)	10000	1840.6 (8)	2871.6 (8)	7.69 (12)
Se(2)	7654.8 (5)	3290.6 (5)	7573.3 (5)	8.93 (9)
Se(3)	10000	-1378.9 (8)	7628.3 (11)	8.60 (10)

Table S5. Anisotropic displacement parameters ($Å^2 \times 10^3$) of $Li_2MgGeSe_4$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ge(1)	7.3 (2)	5.7 (2)	6.3 (2)	0.14 (16)	0	0
Mg(1)	9.7 (11)	10.7 (11)	11.0 (11)	-0.5 (8)	0.7 (10)	0.9 (8)
Li(1)	9.7 (11)	10.7 (11)	11.0 (11)	-0.5 (8)	0.7 (10)	0.9 (8)
Li(2)	17 (6)	27 (7)	20 (7)	12 (5)	0	0
Se(1)	6.00 (18)	11.0 (2)	6.1 (3)	0.52 (17)	0	0
Se(2)	9.23 (14)	7.99 (15)	9.6 (2)	-0.58 (17)	2.09 (16)	0.98 (10)
Se(3)	9.95 (18)	5.92 (19)	9.9 (2)	0.9 (3)	0	0

Table S6. Symmetry, selected bond lengths and angles of crystal data and structural refinements of $Li_2MgGeSe_4$.

Ge(1)-Se(1)	**2.3446 (7)**	**Se(1)-Ge(1)-Se(2)#1**	**108.35 (2)**
Ge(1)-Se(2)	2.3487 (5)	**Se(1)-Ge(1)-Se(2)**	108.35 (2)
Ge (1)-Se(2)#1	2.3487 (5)	**Se(2)#1-Ge(1)-Se(2)**	111.86 (3)
Ge (1)-Se(3)	2.3422 (9)	**Se(3)-Ge(1)-Se(1)**	111.34 (3)
Li(1)#1-Se(1)	2.534 (3)	**Se(3)-Ge(1)-Se(2)**	108.49 (2)
Li(2)#4-Se(1)	2.533 (14)	**Se(3)-Ge(1)-Se(2)#1**	108.49 (2)
Li(1)#7-Se(2)	2.564 (3)	**Se(1)-Mg(1)-Se(2)#2**	105.77 (12)
Li(1)#8-Se(2)	2.557 (4)	**Se(1)-Mg(1)-Se(2)#3**	108.58 (11)
Li(1)#9-Se(3)	2.512 (3)	**Se(2)#3-Mg(1)-Se(2)#2**	106.03 (11)
Li(1)#5-Se(3)	2.512 (3)	**Se(3)#4-Mg(1)-Se(1)**	111.20 (12)
Li(2)#5-Se(3)	2.610 (18)	**Se(3)#4-Mg(1)-Se(2)#2**	112.13 (11)
Li(2)-Se(1)#5	2.533 (14)	**Se(3)#4-Mg(1)-Se(2)#3**	112.74 (12)
Li(2)-Se(2)	2.600 (9)	**Se(1)#5-Li(2)-Se(2)**	110.6 (4)
Li(2)-Se(2)#6	2.600 (9)	**Se(1)#5-Li(2)-Se(2)#6**	110.6 (4)
Li(2)-Se(3)#4	2.610 (18)	**Se(1)#5-Li(2)-Se(3)#4**	107.0 (6)
		Se(2)-Li(2)-Se(2)#6	115.8 (6)
		Se(2)#6-Li(2)-Se(3)#4	106.1 (4)
		Se(2)-Li(2)-Se(3)#4	106.1 (4)

#1 2 − x, +y, +z #2 3/2 − x,1 − y, −1/2 + z #3 + x, +y, −1 + z #4 3/2 − x, −y, −1/2 + z.
#5 3/2 − x, −y, 1/2 + z #6 1 − x, 1 + y, +z #7 +x, +y, +z.
#8 3/2 − x, 1 − y, 1/2 + z #9 1/2 + x, −y, 1/2 + z.

Table S7. Atomic parameters of $Li_2MgSnSe_4$ and $Li_2MgGeSe_4$.

$Li_2MgSnSe_4$			**$Li_2MgGeSe_4$**		
Atom	**Wyckoff Site**	**S.O.F.**	**Atom**	**Wyckoff Site**	**S.O.F.**
Sn(1)	2a		**Ge(1)**	2a	
Mg(1)	4b	0.5	**Mg(1)**	4b	0.5
Li(1)	4b	0.5	**Li(1)**	4b	0.5
Li(2)	2a		**Li(2)**	2a	
Se(1)	2a		**Se(1)**	2a	
Se(2)	2a		**Se(2)**	4b	
Se(3)	4b		**Se(3)**	2a	

Table S8. The refined structural parameters of $Li_2MgSnSe_4$.

$Li_2MgSnSe_4$	
a	8.402 Å
b	7.181 Å
c	6.728 Å
α = β = γ	90 °
V **(Å^3)**	405.932 Å^3
Rwp **(%)**	10.29 %
Rp **(%)**	7.47 %
χ^2	11.70

Table S9. The crystallographic data of Li_2MgMSe_4 (M = Sn, Ge).

$Li_2MgSnSe_4$					
***Pmn*2$_1$ (No.31)**					
Cell parameters					
a **(Å)**	***b*** **(Å)**	***c*** **(Å)**	***α*** **(°)**	***β*** **(°)**	***γ*** **(°)**
8.402	7.181	6.728	90	90	90
Fractional coordinates					
Atoms	**x**		**y**		**z**
Li	0.00000		0.65400		0.40000
Li(0.5)/Mg(0.5)	0.24400		0.82970		0.93200
Sn	0.00000		0.32806		0.91720
Se1	0.00000		0.65740		0.79430
Se2	0.00000		0.32110		1.29290
Se3	0.24679		0.16657		0.79821
$Li_2MgGeSe_4$					
***Pmn*2$_1$ (No.31)**					
Cell parameters					
a **(Å)**	***b*** **(Å)**	***c*** **(Å)**	***α*** **(°)**	***β*** **(°)**	***γ*** **(°)**
8.296	7.007	6.612	90	90	90
Fractional coordinates					
Atoms	**x**		**y**		**z**
Li	0.50000		0.15600		0.65700
Li(0.5)/Mg(0.5)	0.74190		0.32150		0.14280
Ge	1.00000		0.17624		0.64169
Se1	1.00000		0.18406		0.28716
Se2	0.76548		0.32906		0.75733
Se3	1.00000		−0.13789		0.76283

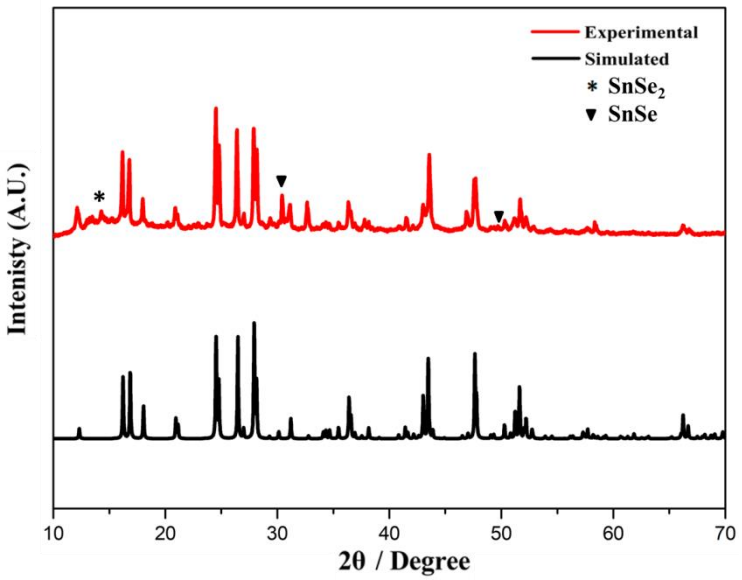

Figure S1. Experimental and calculated PXRD patterns of $Li_2MgSnSe_4$.

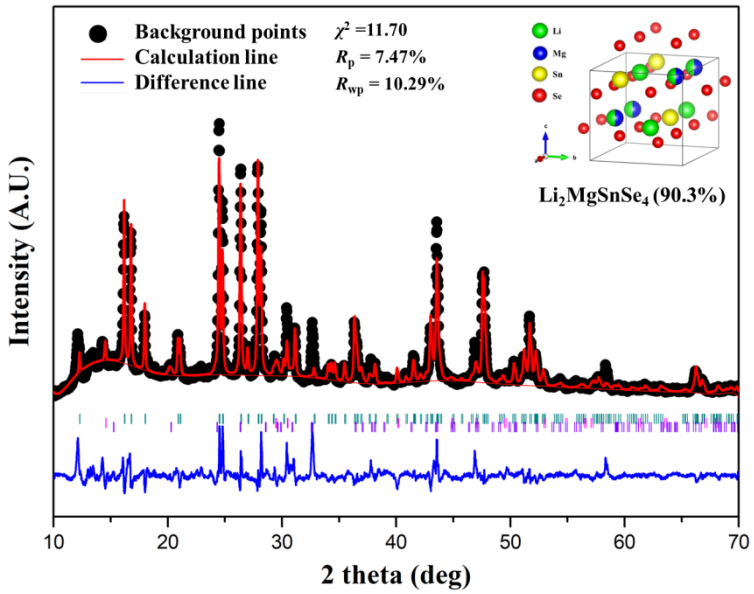

Figure S2. The PXRD Rietveld refinement of the obtained $Li_2MgSnSe_4$ samples.

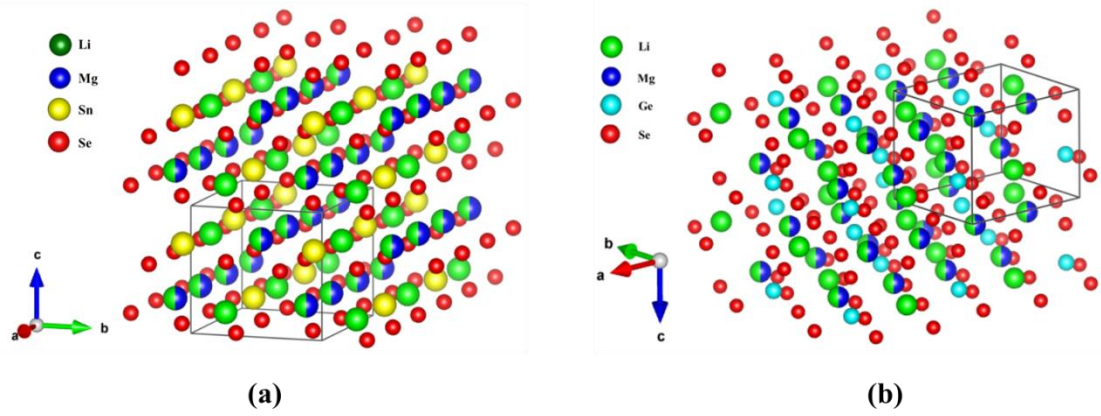

Figure S3. The atomic models of (**a**) $Li_2MgSnSe_4$ and (**b**) $Li_2MgGeSe_4$.