Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information for

First-principles investigation of novel polymorphs of Mg_2C

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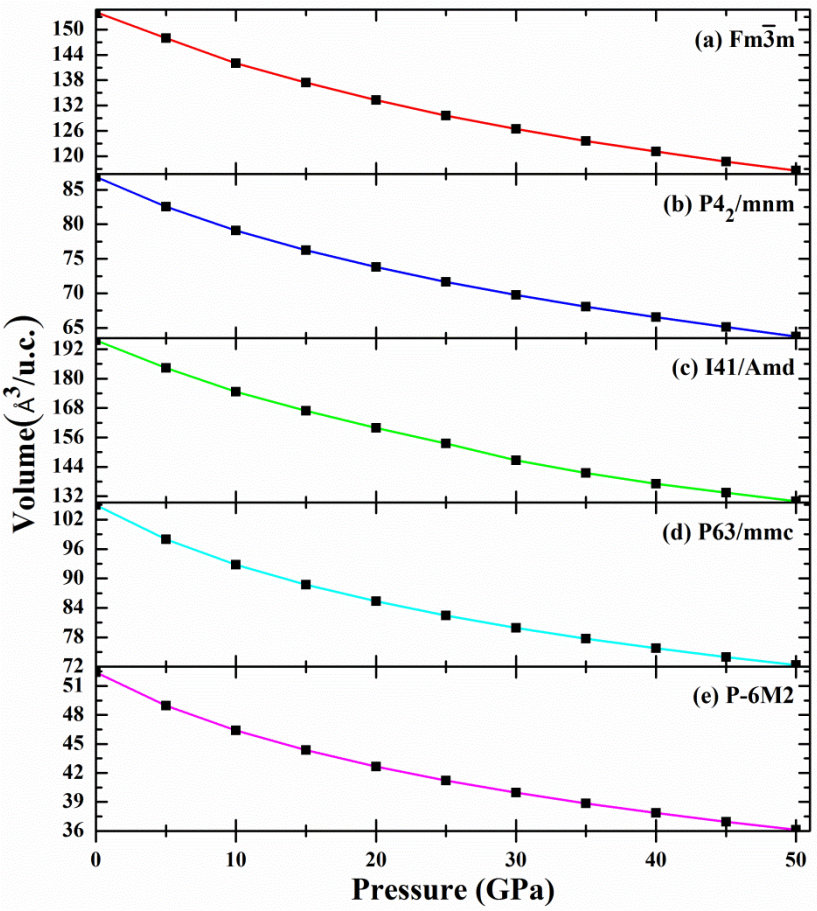


Figure S1: The LDA functional calculated pressure dependence of cell volume for various Mg_2C polymorphs.

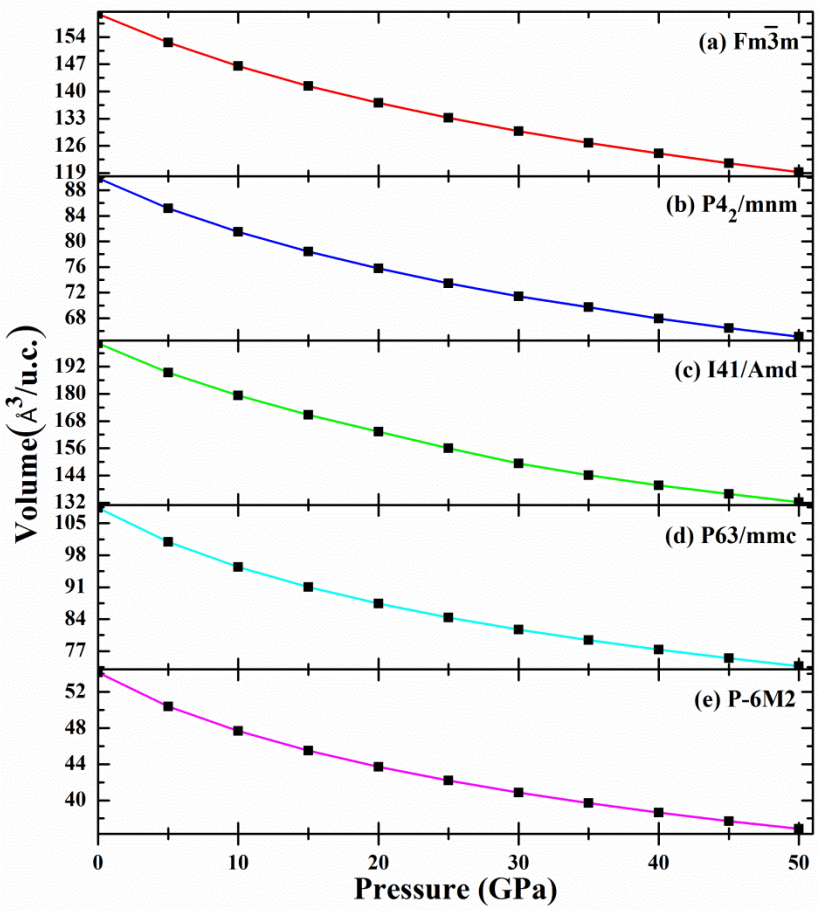


Figure S2: The PBEsol functional calculated pressure dependence of cell volume for various Mg_2C polymorphs.

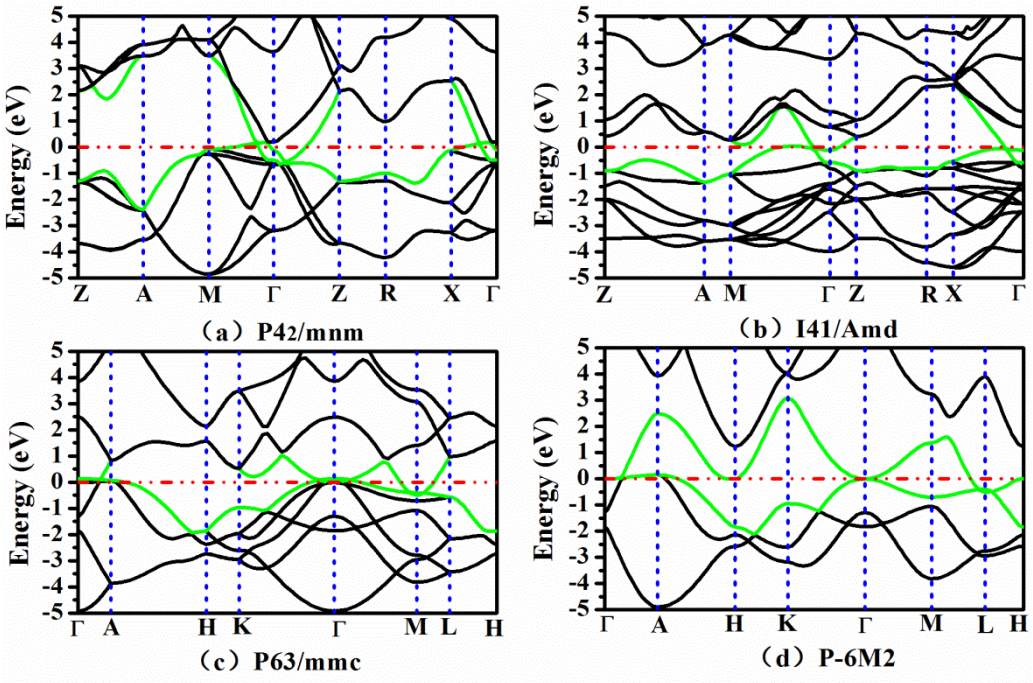


Figure S3: Calculated band structure for the newly proposed phases by LDA.

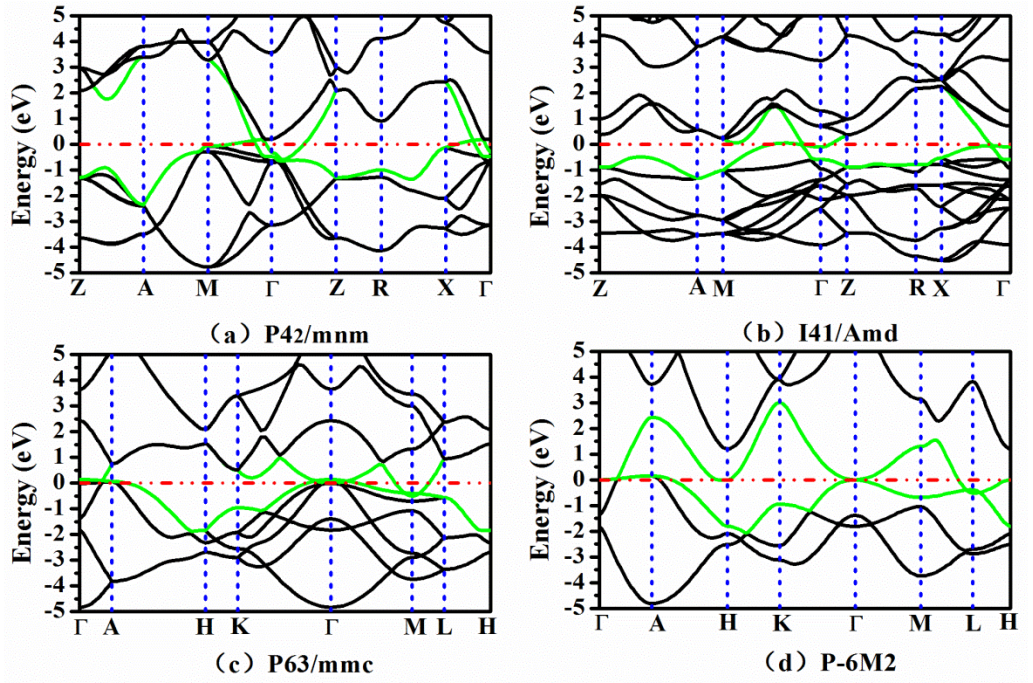
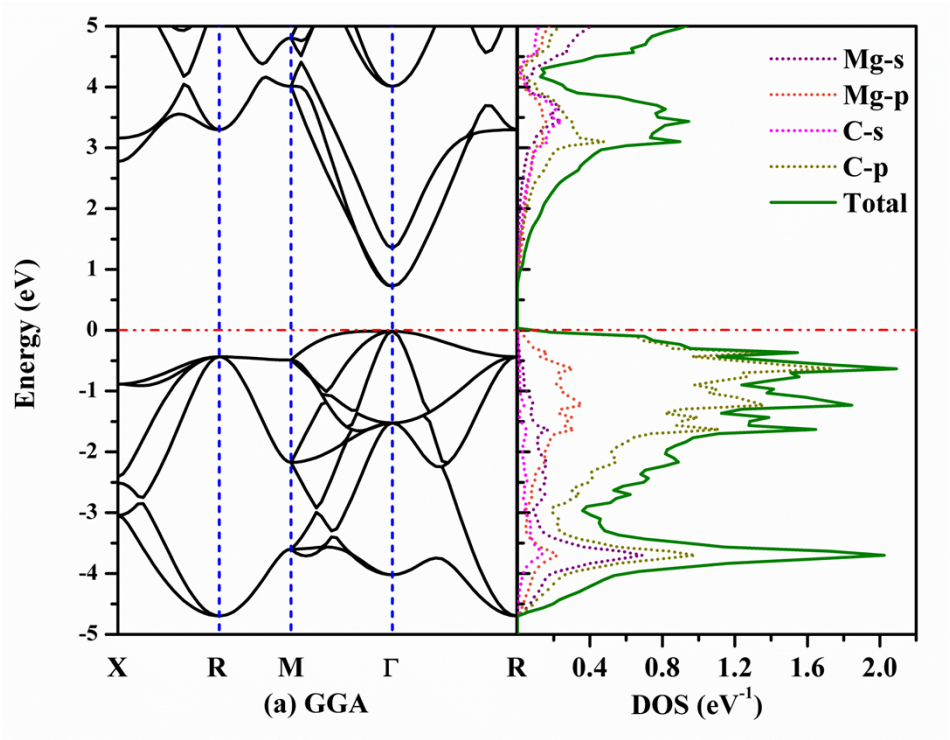
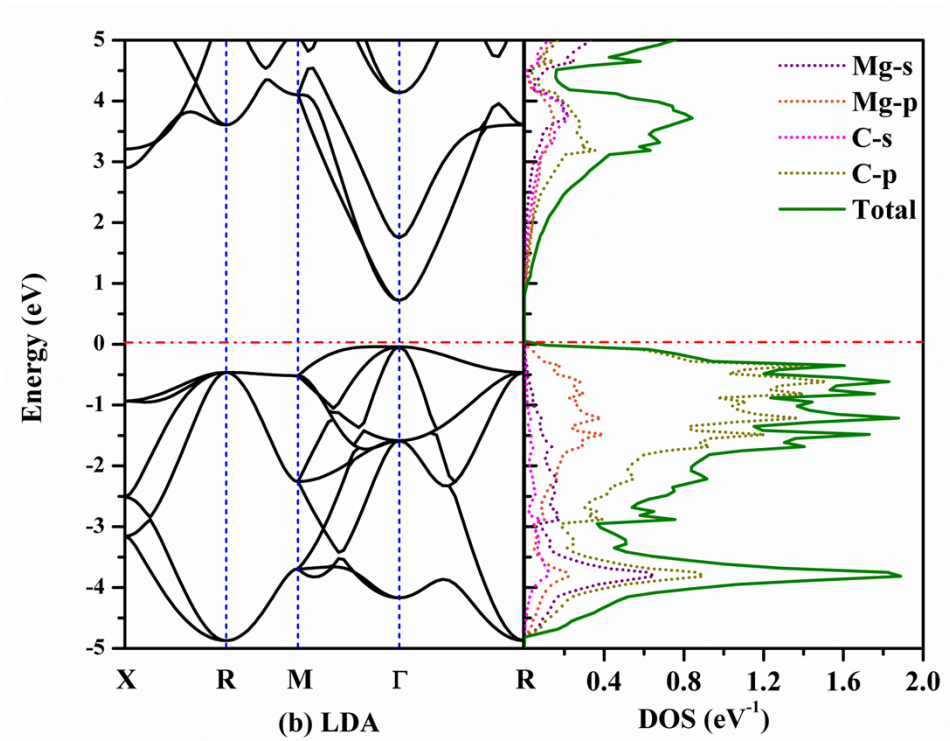


Figure S4: Calculated band structure for the newly proposed phases by PBEsol.


Energy (eV)
5
4
3
2
1
0
-1
-2
-3
-4
-5
X
R
M
Γ
R
0.4
0.8
1.2
1.6
2.0
DOS (eV-1)
Mg-s
Mg-p
C-s
C-p
Total

(a) GGA


Energy (eV)
5
4
3
2
1
0
-1
-2
-3
-4
-5
X
R
M
Γ
R
0.4
0.8
1.2
1.6
2.0
DOS (eV-1)
Mg-s
Mg-p
C-s
C-p
Total

(b) LDA

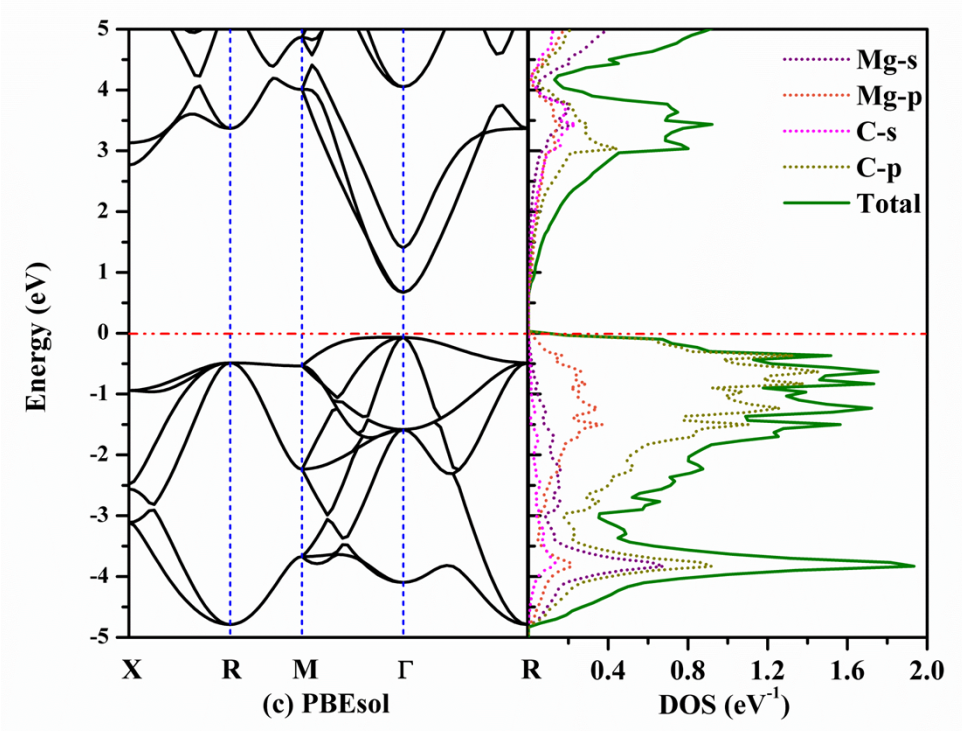


Figure S5: Calculated band structure for the known cubic phase by (a) GGA, (b) LDA and (c) PBEsol. The band gap is calculated to be 0.7392 eV, 0.7607 eV and 0.7407 eV, respectively.

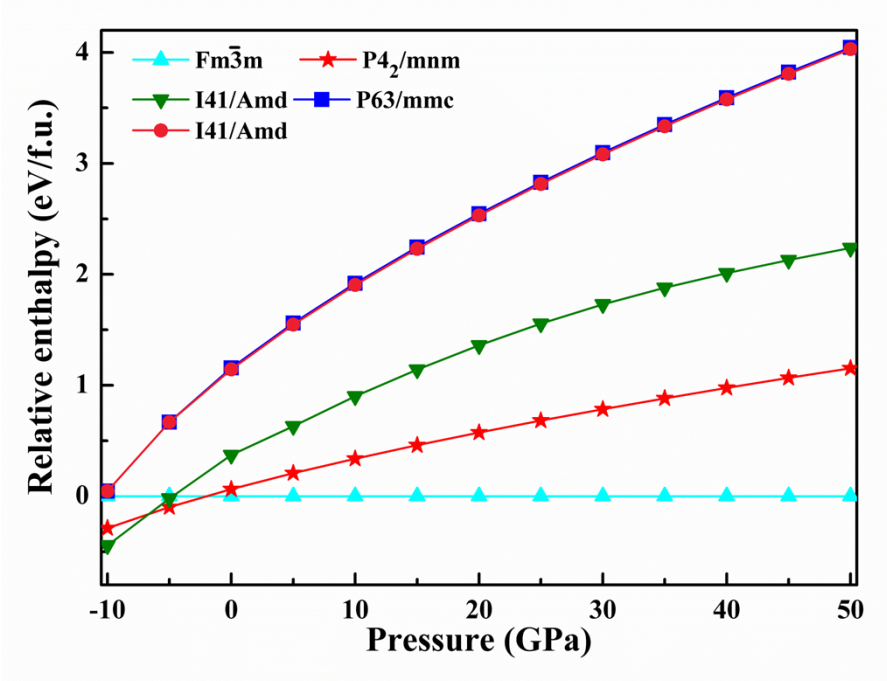


Figure S6: The LDA calculated enthalpy curves (relative to the $Fm\bar{3}m$ phase) as a function of pressure for different Mg_2C polymorphs.

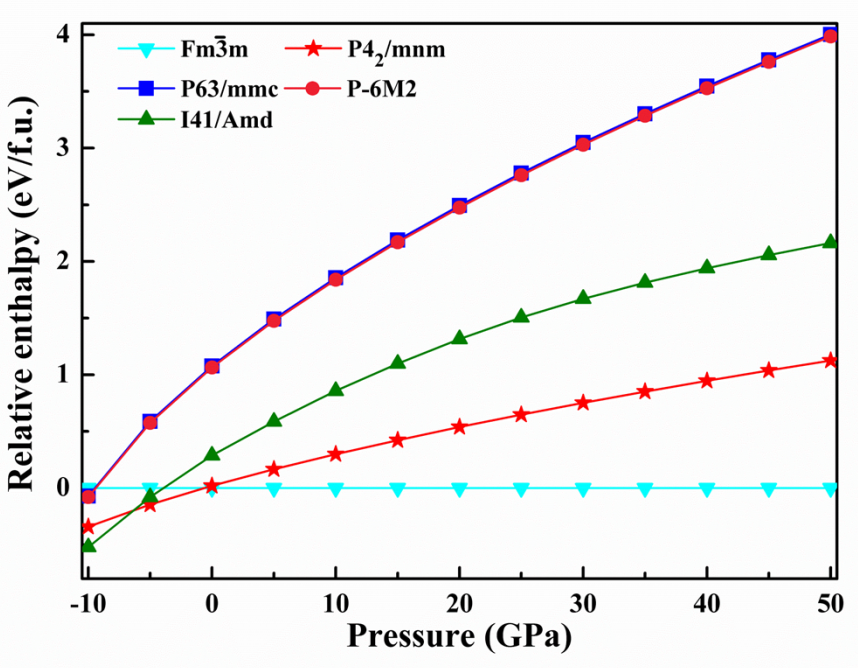


Figure S7: The GGA-PBEsol calculated enthalpy curves (relative to the $Fm\bar{3}m$ phase) as a function of pressure for different Mg_2C polymorphs.

Table S1 The thermodynamic stability of the newly proposed phases and the known cubic phase relative to Mg (*hcp*) and MgC_2 (space group *P42/mnm*, No. 136)

$1/2MgC_2+3/2Mg \rightarrow Mg_2C$	GGA	LDA	PBEsol
Fm-3m-Mg_2C	0.122240493	**-0.173083217**	0.886870015
I41/Amd-Mg_2C	0.325755293	0.1549934	1.165780553
$P4_2$/mnm-Mg_2C	0.099081875	**-0.10918856**	0.90723222
P63-Mg_2C	1.083048635	0.98297021	1.964644355
P-6M2-Mg_2C	1.068844585	0.96946921	1.95070208

Unit: eV

Table S2 The thermodynamic stability of the newly proposed phases and the known cubic phase relative to Mg (*hcp*) and α-Mg_2C_3 (space group *pnnm*, No. 58)

$1/3\alpha$-$Mg_2C_3+4/3Mg \rightarrow Mg_2C$	GGA	LDA	PBEsol
Fm-3m-Mg_2C	0.482436693	0.306524144	0.426707443
I41/Amd-Mg_2C	0.685951493	0.634600762	0.705617981
$P4_2$/mnm-Mg_2C	0.459278075	0.370418802	0.447069648
P63-Mg_2C	1.443244835	1.462577572	1.504481783
P-6M2-Mg_2C	1.429040785	1.449076572	1.490539508

Unit: eV

Table S3 The thermodynamic stability of the newly proposed phases and the known cubic phase relative to Mg (*hcp*) and β-Mg_2C_3 (space group *C2/m*, No. 12)

$1/3\beta$-$Mg_2C_3+4/3Mg \rightarrow Mg_2C$	GGA	LDA	PBEsol
Fm-3m-Mg_2C	0.401367777	0.274169291	0.391706213
I41/Amd-Mg_2C	0.604882578	0.634600762	0.705617981
$P4_2$/mnm-Mg_2C	0.37820916	0.338063948	0.412068418
P63-Mg_2C	1.36217592	1.430222718	1.469480553
P-6M2-Mg_2C	1.34797187	1.416721718	1.455538278

Unit: eV