Electronic Supplementary Information:

Rapid, Energy-Efficient and Pseudomorphic Microwave-Induced-Metal-Plasma (MIMP) Synthesis of Mg_2Si and Mg_2Ge

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1. Supplementary SEM/EDS and SAED Results for Mg_2Si

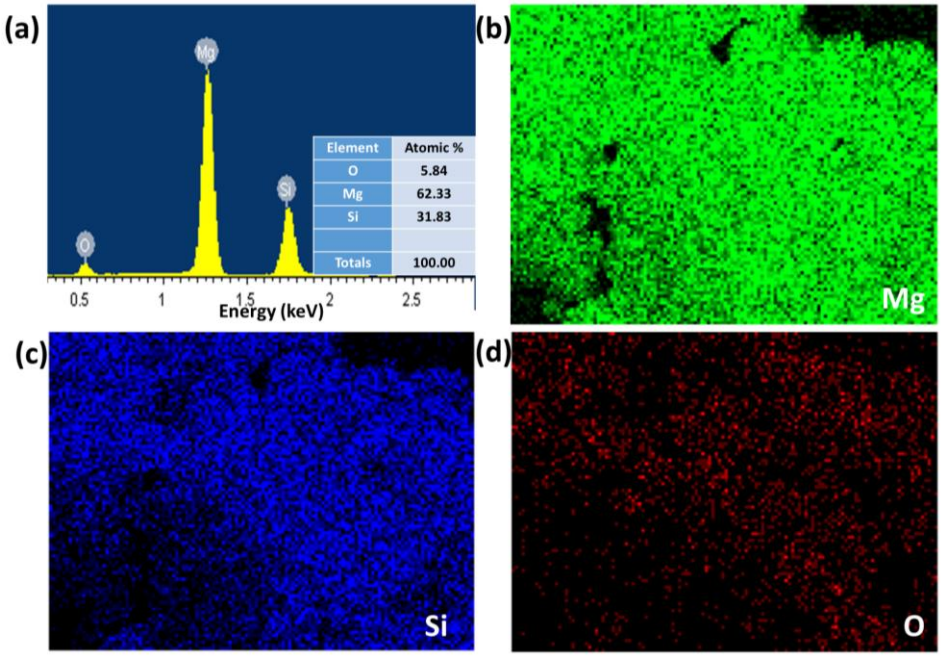

Figure S1. (a) The representative EDX spectrum corresponding to the SEM image in Figure 2d; and the corresponding **(b-d)** Elemental mappings of Mg, Si and O, respectively.

Table S1. Indexed lattice planes from the SAED patterns shown in Figure 1h.

Diffraction No.	Indexed Diffraction Distance / nm	Lattice Plane – Mg_2Si
1	0.230	(220)
2	0.190	(311)
3	0.150	(331)
4	0.120	(511)
5	0.106	(531), (600)
6	0.094	(533), (622)

2. Structure of the Nanoporous Ge Reactant Powders

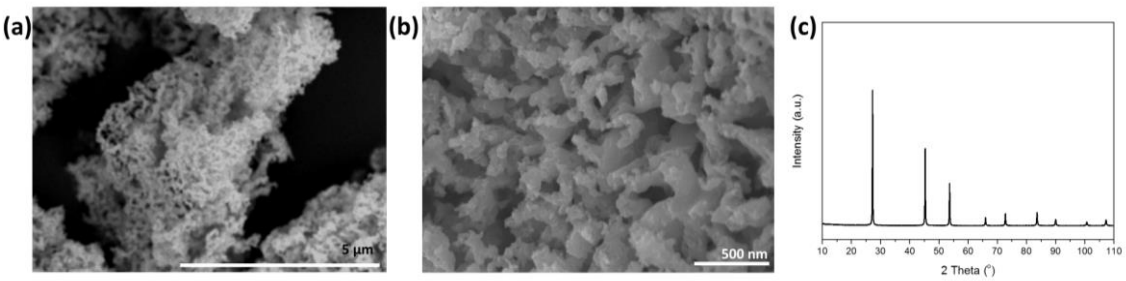

Figure S2. (a, b) SEM images and (c) PXRD patterns of the nanoporous Ge reactant powders.

3. Mg_2Ge synthesized from Mg and Ge, irradiated for 30 s.

Table S2. Crystallographic data obtained from the Rietveld refinement of the MIMP-synthesised product of Mg_2Ge with an irradiation time of 30 s (see also Figure 3a).

Chemical Formula	**Mg_2Ge**	**Mg**	**Ge**
Crystal System	Cubic	Hexagonal	Cubic
Space Group	*Fm*-3*m* (225)	$P6_3/mmc$ (194)	*Fd*-3*m* (227)
Lattice Parameter / Å	6.3935(2)	3.2124(5) 5.2136(17)	5.6568 [a]
Cell Volume / $Å^3$	261.349(22)	46.593(14)	181.014 [a]
Formula Weight / g mol^{-1}	484.800	48.610	580.720
Formula Units, *Z*	4	2	8
Calculated Density / g cm^{-3}	3.080	1.732	5.327
Phase Fraction / wt.%	94.3(3)	4.1(3)	1.5(1)
No. of Variables		19	
No. of Observations		2090	
wRp		0.2646	
Rp		0.1788	
χ^2		1.960	

[a.] Not refined.

Table S3. Atomic parameters for MIMP-synthesised Mg_2Ge (irradiated for 30 s).

Atom	**Site**	***x***	***y***	***z***	**100 × U_{iso} / $Å^2$**	**SOF [a]**
Mg	8*c*	0.25	0.25	0.25	2.54(18)	1
Ge	4*a*	0	0	0	2.24(12)	1

[a.] Not refined.

4. MIMP-synthesised Mg_2Ge from Commercial Bulk Ge Powders

In order to investigate between the premise that the reaction between Mg and nanoporous Ge was pseudomorphic, a supplementary MIMP synthesis was conducted. Commercial Ge powders (Trace metal basis, 99.999%, Acros Organics) were initially ground manually using a mortar and pestle. Mg powder (35 mg) and as-ground Ge powder (45 mg) were mixed thoroughly. The MW synthesis was performed with an incident power of 200 W for an irradiation time of 90 s under a static vacuum of $P < 10^{-6}$ mbar. The Rietveld refinement results (Figure S3a; Table S4) confirmed the *anti*fluorite structure of Mg_2Ge with a lattice parameter of a = 6.3894(4) Å. The refined phase fraction of the main phase was 95.9(4) wt.%, with the presence of small amounts of MgO (3.2(2) wt.%) and Ge (0.9(6) wt.%) impurity phases indicated. In contrast to the Mg_2Ge sample synthesised from nanoporous Ge starting material (Figures 4a,b), the STEM image in Figure S3b showed that the Mg_2Ge produced from commercial Ge was composed of dense bulk particles and was not porous.

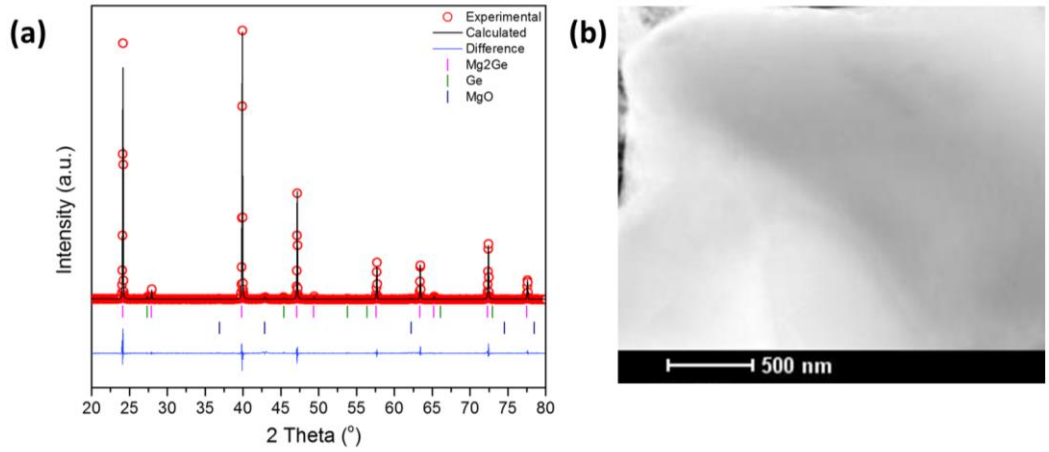

Figure S3. (a) Profile plot of the Rietveld refinement against PXRD data, and **(b)** a STEM image of the Mg_2Ge product as obtained from the MW synthesis experiment using a commercial Ge starting material, illustrating the relatively large particle size obtained.

Table S4. Crystallographic data obtained from the Rietveld refinement of the MIMP-synthesised Mg_2Ge synthesised from commercial Ge powder (see also Figure S3a).

Chemical Formula	**Mg_2Ge**	**MgO**	**Ge**
Crystal System	Cubic	Cubic	Cubic
Space Group	*Fm*-3*m* (225)	*Fm*-3*m* (225)	*Fd*-3*m* (227)
Lattice Parameter / Å	6.3894(4)	4.2170 [a]	5.6568 [a]
Cell volume / $Å^3$	260.85(5)	74.991[a]	181.014 [a]
Formula Weight / g mol^{-1}	484.800	161.216	580.720
Formula Units, *Z*	4	4	8
Calculated Density / g cm^{-3}	3.086	3.570	5.327
Phase Fraction / wt.%	95.9(4)	3.2(2)	0.9(6)
No. of Variables		27	
No. of Observations		2093	
wRp		0.2071	
Rp		0.1397	
χ^2		0.2199	

[a.] Not refined.

Table S5. Atomic parameters for MIMP-synthesised Mg_2Ge from commercial Ge powder (see also Figure S3a).

Atom	**Site**	***x***	***y***	***z***	**100 × U_{iso} / $Å^2$**	**SOF [a]**
Mg	8*c*	0.25	0.25	0.25	2.77(14)	1
Ge	4*a*	0	0	0	2.26(9)	1

[a.] Not refined.