# *Supporting information*

# A new tilt and an old twist on the nickel arsenide structure-type: synthesis and characterisation of the quaternary transition-metal cyanamides $A_2MnSn_2(NCN)_6$ ($A$ = Li and Na)

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**Table S1.** Crystallographic data and fractional coordinates for $Li_2MnSn_2(NCN)_6$. Standard deviations are given in parentheses.

| Atom | Wyckoff site | *x* | *y* | *z* | $U_{iso}$($10^2$ ×Å$^2$) |
|---|---|---|---|---|---|
| Li1 | 2*d* | ⅓ | ⅔ | ½ | 1.43(3) |
| Mn | 1*b* | 0 | 0 | ½ | 2.81(13) |
| Sn1 | 2*c* | ⅓ | ⅔ | 0 | 1.43(3) |
| C | 6*k* | 0.646(3) | 0 | 0.2554(8) | 2.48(16) |
| N1 | 6*k* | 0.6842(13) | 0 | 0.3753(7) | " |
| N2 | 6*k* | 0.5998(13) | 0 | 0.1211(7) | " |
| Trigonal, $P\bar{3}1m$ (No. 162), $Z$ = 1, $a$ = 5.85976(6) Å, $c$ = 9.5466(2) Å; $R_{wp}$ = 5.31 %, $R_p$ = 4.17 %, $\chi^2$ = 1.203, 34 variables | | | | | |

**Table S2.** Infrared frequencies assigned to characteristic vibrations for $Na_2MnSn_2(NCN)_6$, $Li_2MnSn_2(NCN)_6$ and [NaCl]-type MnNCN.

| | $Na_2MnSn_2(NCN)_6$ | $Li_2MnSn_2(NCN)_6$ | [NaCl]-type MnNCN |
|---|---|---|---|
| δ (NCN) | 606, 707 | 608, 711 | 647 |
| $\nu_s$ (NCN) | 1200, 1284 | 1200, 1288 | |
| $\nu_{as}$ (NCN) | 2055, 21455 | 2049, 2166 | 2005 |

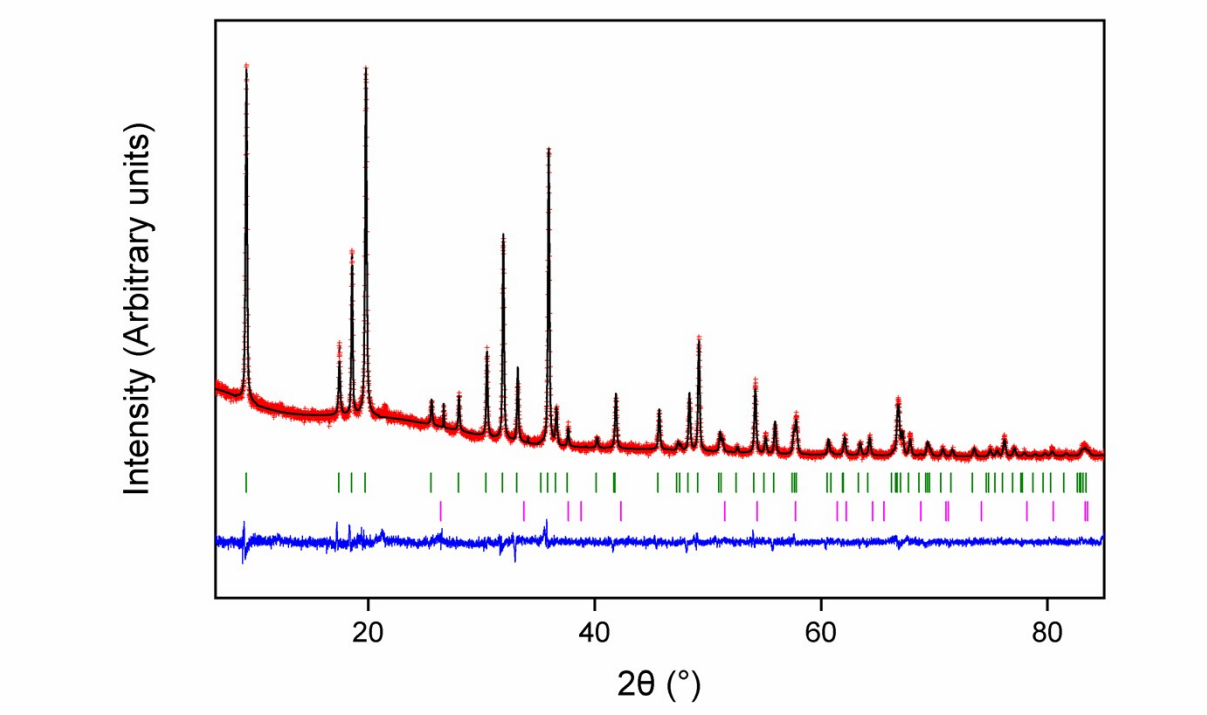


**Fig. S1** Rietveld fit of $Li_2MnSn_2(NCN)_6$ to PXRD data, showing observed (red), calculated (black) and difference (blue) intensities. Bragg positions of $Li_2MnSn_2(NCN)_6$ (green) and $SnO_2$ (pink) are denoted by vertical markers.

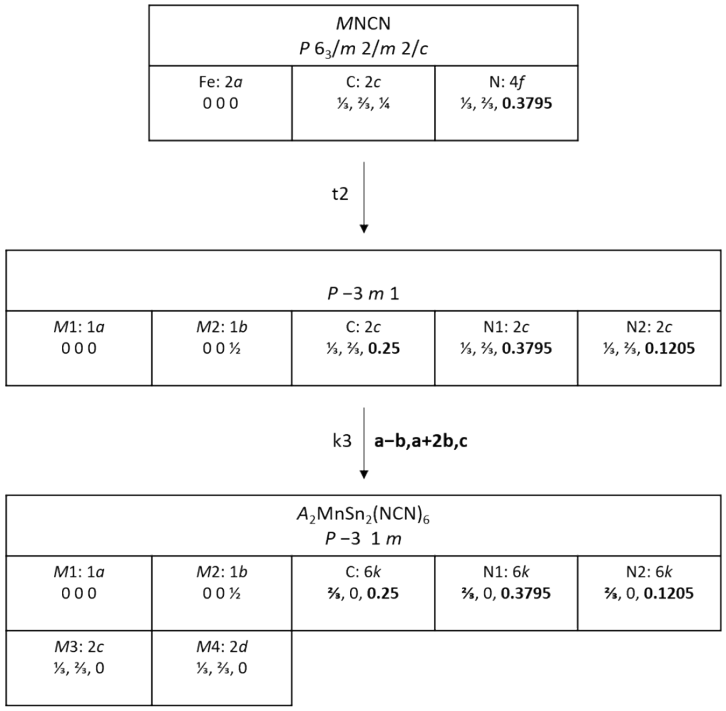


**Fig. S2** Group-subgroup relationship from *M*NCN ($P6_3/mmc$) to $A_2MnSn_2(NCN)_6$ ($P\bar{3}1m$).

**Table S3.** Normalized mode amplitudes of $Na_2MnSn_2(NCN)_6$ (norm. factor: √3).

| *K*-vector | Irrep | Direction | Isotropy Subgroup | Dimension | Amplitude (Å) |
|---|---|---|---|---|---|
| (0,0,0) | $\Gamma_1^+$ | (*a*) | $P6_3/mmc$ (194) | 1 | 0.1188 |
| (0,0,0) | $\Gamma_3^+$ | (*a*) | $P\bar{3}1m$ (164) | 2 | 0.1007 |
| (⅓,⅓,0) | $K_1$ | (*a*,0) | $P6_3/mcm$ (193) | 2 | 0.2910 |
| (⅓,⅓,0) | $K_2$ | (0,*a*) | $P\bar{3}1m$ (162) | 1 | 0.5779 |

**Table S4.** Normalized mode amplitudes of $Li_2MnSn_2(NCN)_6$ (norm. factor: √3).

| *K*-vector | Irrep | Direction | Isotropy Subgroup | Dimension | Amplitude (Å) |
|---|---|---|---|---|---|
| (0,0,0) | $\Gamma_1^+$ | (*a*) | $P6_3/mmc$ (194) | 1 | 0.0458 |
| (0,0,0) | $\Gamma_3^+$ | (*a*) | $P\bar{3}1m$ (164) | 2 | 0.0806 |
| (⅓,⅓,0) | $K_1$ | (*a*,0) | $P6_3/mcm$ (193) | 2 | 0.336 |
| (⅓,⅓,0) | $K_2$ | (0,*a*) | $P\bar{3}1m$ (162) | 1 | 0.4945 |

**Table S5.** Normalized mode amplitudes of $PbSb_2O_6$ (norm. factor: √3).

| *K*-vector | Irrep | Direction | Isotropy Subgroup | Dimension | Amplitude (Å) |
|---|---|---|---|---|---|
| (0,0,0) | $\Gamma_3^+$ | (*a*) | $P\bar{3}1m$ (164) | 1 | 0.4242 |
| (⅓,⅓,0) | $K_1$ | (*a*,0) | $P6_3/mcm$ (193) | 1 | 0.3930 |