

# Supplementary Materials: Synthesis and Structural Characterization of $\text{Ba}_7\text{Li}_{11}\text{Bi}_{10}$ and $\text{AE}_4(\text{Li}, \text{Tr})_7\text{Pn}_6$ ( $\text{AE} = \text{Sr}, \text{Ba}, \text{Eu}$ ; $\text{Tr} = \text{Ga}, \text{In}$ ; $\text{Pn} = \text{Sb}, \text{Bi}$ )

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**Table S1.** Selected crystal structure data and refinement parameters for  $\text{EuLi}_{2.58}\text{In}_{0.42(2)}\text{Bi}_2$ .

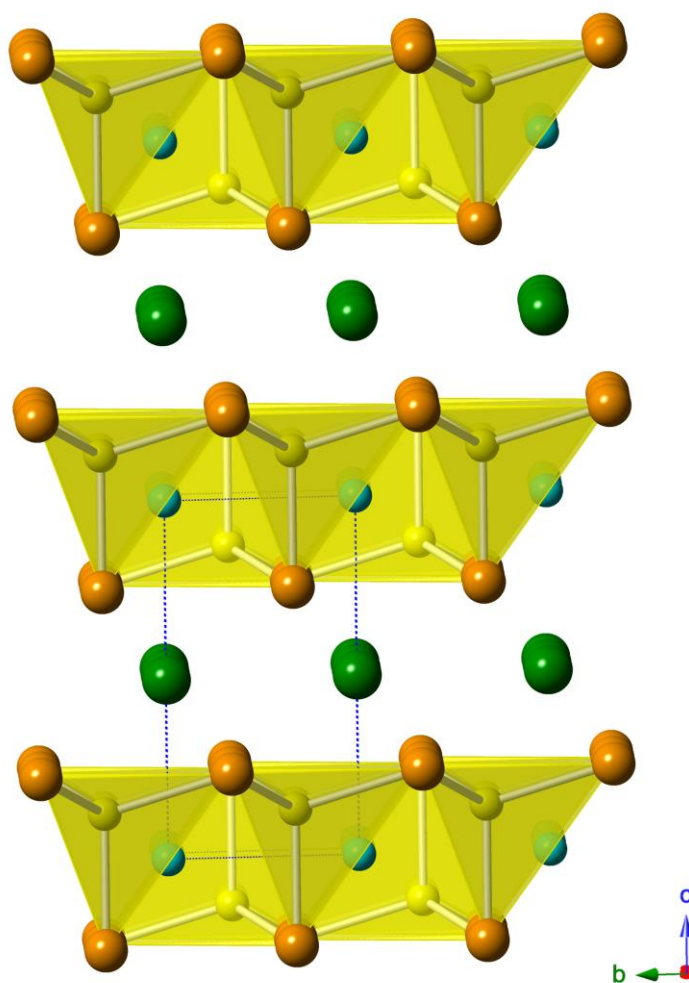
Empirical formula	$\text{EuLi}_{2.58}\text{In}_{0.42(2)}\text{Bi}_2$
fw, g mol <sup>-1</sup>	633.89
Space group, <i>Z</i>	$P\bar{3}m1$ (No.164), 1
$\lambda$ , Å	0.71073
<i>T</i> , K	200(2)
<i>a</i> , Å	4.7671(6)
<i>c</i> , Å	7.725(2)
<i>V</i> , Å <sup>3</sup>	152.00(8)
$\rho_{\text{calc}}$ , g cm <sup>-3</sup>	6.93
$\mu_{\text{Mo-K}\alpha}$ , cm <sup>-1</sup>	692.5
GOF on <i>F</i> <sup>2</sup>	1.157
<i>R</i> <sub>1</sub> ( <i>I</i> > 2σ( <i>I</i> )) <sup>b</sup>	0.0317
<i>R</i> <sub>1</sub> (all data) <sup>b</sup>	0.0337
<i>wR</i> <sub>2</sub> ( <i>I</i> > 2σ( <i>I</i> )) <sup>b</sup>	0.0747
<i>wR</i> <sub>2</sub> (all data) <sup>b</sup>	0.0759
Largest peak/hole, e <sup>-</sup> Å <sup>-3</sup>	4.54/−2.77

<sup>b</sup>  $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$ ;  $wR_2 = [\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]]^{1/2}$ , where  $w = 1/[\sigma^2(F_o^2) + (0.0485P)^2]$ , and  $P = (F_o^2 + 2F_c^2)/3$ .

**Table S2.** Final refined positional coordinates and displacement parameters for  $\text{EuLi}_{2.58}\text{In}_{0.42(2)}\text{Bi}_2$ .

Atom	Wyckoff site	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^a/U_{\text{eq}}^b$ , Å <sup>2</sup>	Occupancy
Eu1	1 <i>b</i>	0	0	1/2	0.0155(5)	1
Bi1	2 <i>d</i>	1/3	2/3	0.2444(1)	0.0165(5)	1
Li1/In	2 <i>d</i>	1/3	2/3	0.8642(8)	0.019(2) <sup>a</sup>	0.79/0.21(1)
Li2	1 <i>a</i>	0	0	0	0.013(2) <sup>a</sup>	1

<sup>a</sup> Isotropic refinement; <sup>b</sup>  $U_{\text{eq}}$  is defined as one third of the trace of the orthogonalized  $U_{ij}$  tensor.



**Figure S1.** Polyhedral representation of the crystal structure of  $\text{EuLi}_{2.58}\text{In}_{0.42(2)}\text{Bi}_2$ , isotypic to  $\text{LaLi}_3\text{Sb}_2$ , a filled variant of the  $\text{CaAl}_2\text{Si}_2$ -type, viewed down the crystallographic  $a$ -axis. The unit cell is outlined. Eu atoms are shown in medium-green, the Bi atoms in orange, Li1/In atoms in yellow, while Li2 atoms are depicted light-blue. Note that irrespective of the different structure/symmetry, In and Li are disordered on the same location as in the slabs with same topology in the  $\text{Ba}_4(\text{Li}_{1-x}\text{In}_x)_7\text{Sb}_6$ ,  $\text{Ba}_4(\text{Li}_{1-x}\text{In}_x)_7\text{Bi}_6$ , and  $\text{Eu}_4(\text{Li}_{1-x}\text{In}_x)_7\text{Bi}_6$  structures. The octahedral position, Li2 in both cases appears to be devoid of disorder, even though refining the light Li in close proximity of the heavy Bi was not trivial in some of the worked-out datasets.