

# Two new Ba/Li gallides with [Ga<sub>2</sub>] dumbbells:

## Ba<sub>2</sub>Li<sub>2</sub>[Ga<sub>2</sub>] and BaLi<sub>8</sub>[Ga<sub>2</sub>][Ga<sub>4</sub>]

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In the ternary system Ba–Li–Ga, only the two compounds **C1** (Ba<sub>3</sub>Li[Ga<sub>5</sub>] [2], *nido*-octahedra [Ga<sub>5</sub>]) and **C2** [1], corrected to be the 3:8 electride Ba<sub>3</sub>□Li<sub>4</sub>[Ga<sub>4</sub>] [3], tetrahedra [Ga<sub>4</sub>]<sup>6−</sup>) were previously known in the literature. During attempts to reproduce **C2**, we recently obtained the cluster compound Ba<sub>6</sub>Li<sub>2</sub>[Li@Li<sub>3</sub>Ga<sub>3</sub>], **C3**, in addition [3]. The two new title compounds **C4** and **C5** were also yielded from Li-rich samples (**S2**, **S3**). Further new trigonal and hexagonal structures, like e.g. the Ca<sub>3</sub>Cu<sub>6</sub>Al<sub>5</sub>-type phase **C7** [4], Ba<sub>3</sub>(Li/Ga)<sub>40</sub> (**C6**) and some members of the 3:8 to 3:10 series (magenta bar) will be presented elsewhere [3].

The structures of the Ba–Li–Ga phases can alternatively be described as

- mixed Ba/Li gallides (i.e. ZINTL phases) or
- tetrahedra packings of polar Li/Ga polyanions (i.e. FRANK-KASPER phases).

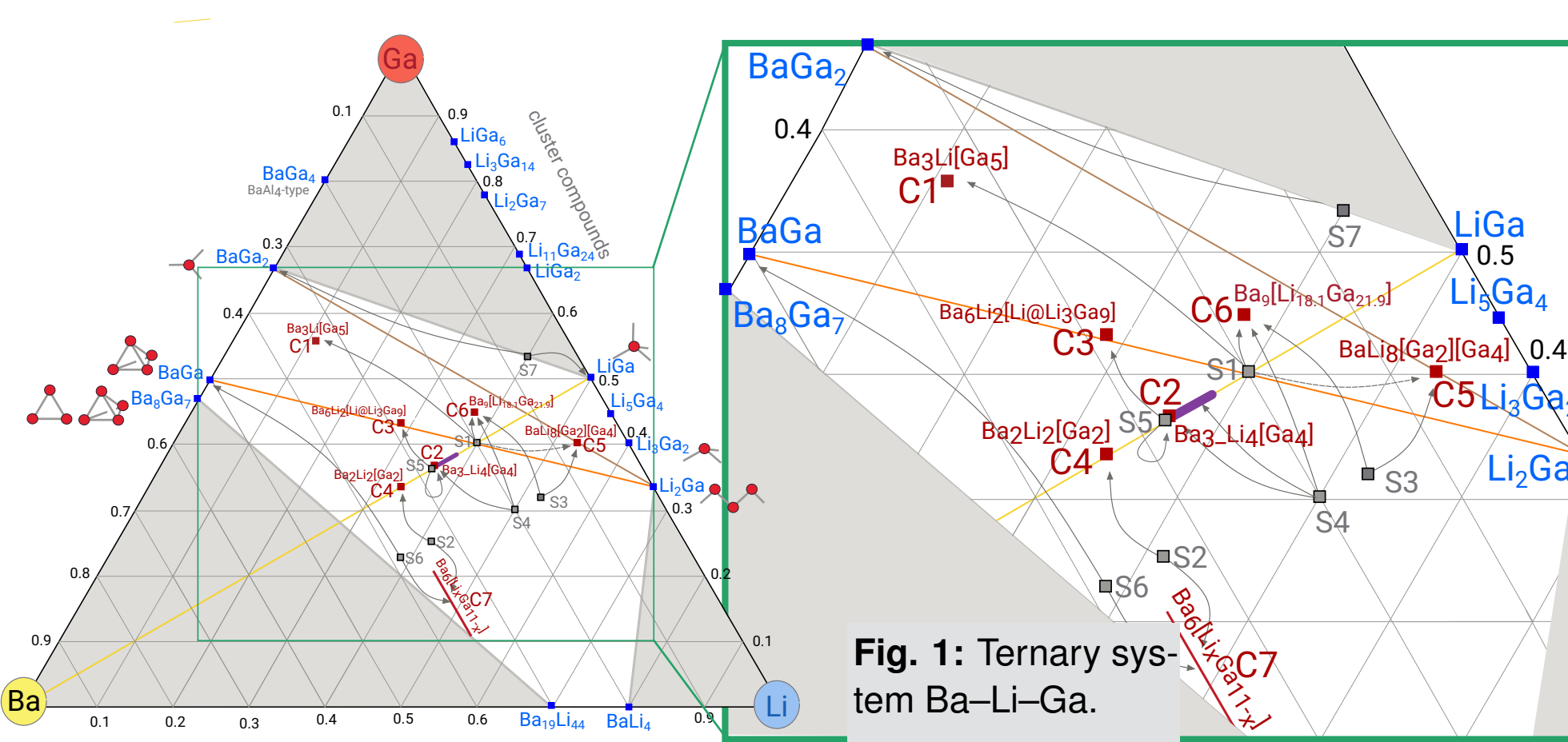


Fig. 1: Ternary system Ba–Li–Ga.

### Crystal structure of Ba<sub>2</sub>Li<sub>2</sub>[Ga<sub>2</sub>] (**C4**)

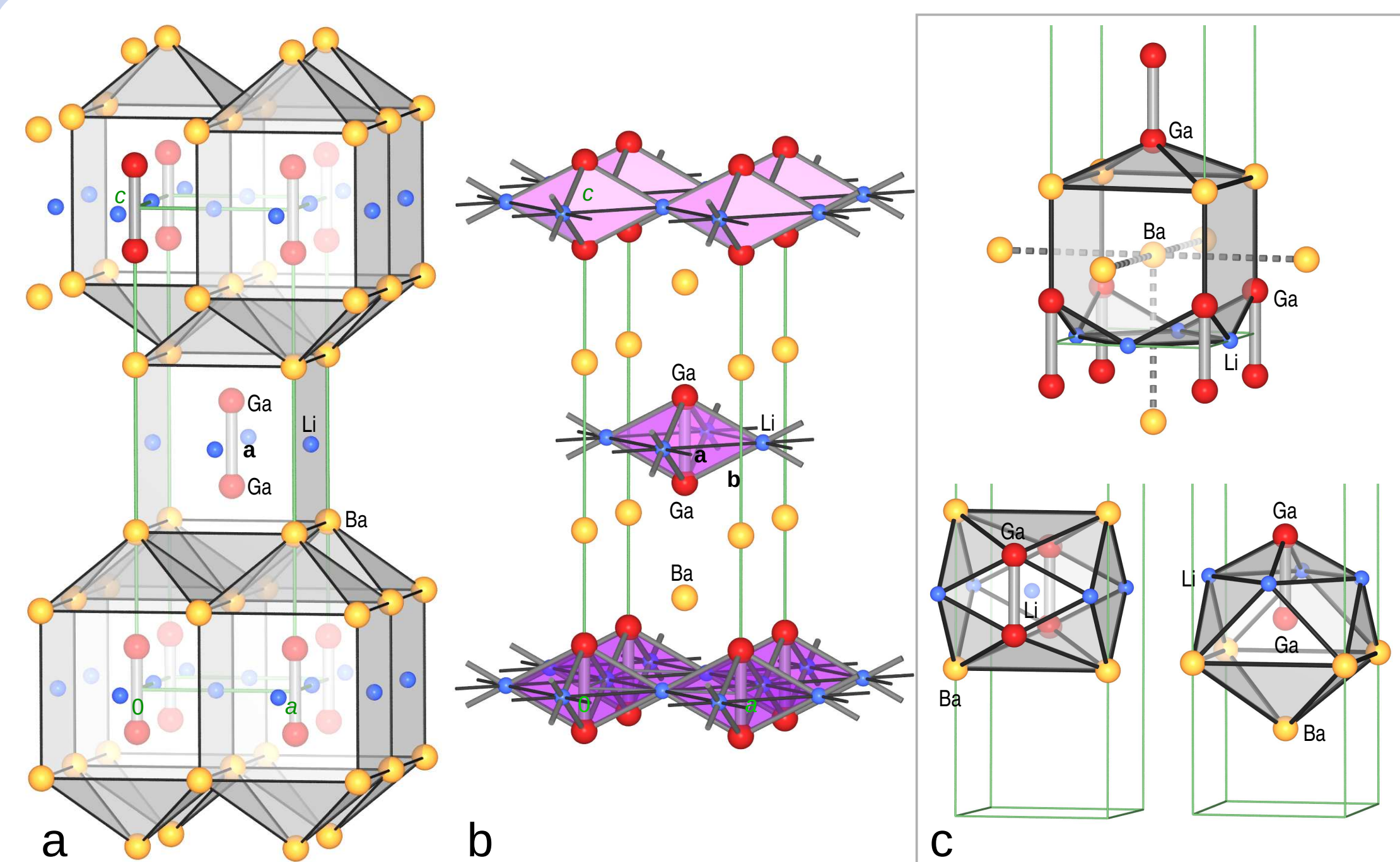


Fig. 2: Unit cell of the structure of Ba<sub>2</sub>Li<sub>2</sub>[Ga<sub>2</sub>] (a,b) and coordination polyhedra of all atoms (c).

The tetragonal structure of Ba<sub>2</sub>Li<sub>2</sub>[Ga<sub>2</sub>] (**C4**, crystal data Table 3 and 4) contains [Ga<sub>2</sub>] dumbbells as sole gallide anions, which are oriented along [001]. They are surrounded by double-capped square prisms of 10 Ba cations, with the remaining four faces of the prisms centered by four additional Li cations (gray polyhedra [(Ga<sub>2</sub>)@Li<sub>4</sub>Ba<sub>10</sub>] in Fig. 2a). Highlighting the overall polar Li/Ga polyanion, the structure can alternatively be considered as a defect K<sub>2</sub>[NiF<sub>4</sub>]-type derivative, Ba<sub>2</sub>[□Li<sub>2</sub>Ga<sub>2</sub>], containing layers of flat edge-sharing octahedra [Ga<sub>2</sub>Li<sub>4</sub>/2] (magenta polyhedra, Fig. 2b) with a central [Ga<sub>2</sub>] unit.

Table 1: Interatomic distances [pm] in the crystal structure of Ba<sub>2</sub>Li<sub>2</sub>[Ga<sub>2</sub>].

| Atoms | Distance | Mult.     | CN      | Atoms | Distance | Mult.      | Label | CN    |
|-------|----------|-----------|---------|-------|----------|------------|-------|-------|
| Ba    | - Ga     | 349.20(8) |         | Li    | - Ga     | 277.04(4)  | 4×    | b     |
|       | - Li     | 353.58(4) | 4×      |       | - Li     | 346.43(4)  | 4×    |       |
|       | - Ga     | 368.49(5) | 4×      |       | - Ba     | 353.58(4)  | 4×    |       |
|       | - Ba     | 412.33(5) | 4×      |       |          |            |       | 4+4+4 |
|       | - Ba     | 489.93(6) | 4×      | Ga    | - Ga     | 258.78(12) |       | a     |
|       | - Ba     | 509.95(9) |         |       | - Li     | 277.04(4)  | 4×    | b     |
|       |          |           | (5+4)+9 |       | - Ba     | 349.20(8)  |       |       |
|       |          |           |         |       | - Ba     | 368.49(5)  | 4×    |       |
|       |          |           |         |       |          |            |       | 1+4+5 |

### Crystal structure of BaLi<sub>8</sub>[Ga<sub>2</sub>][Ga<sub>4</sub>] (**C5**)

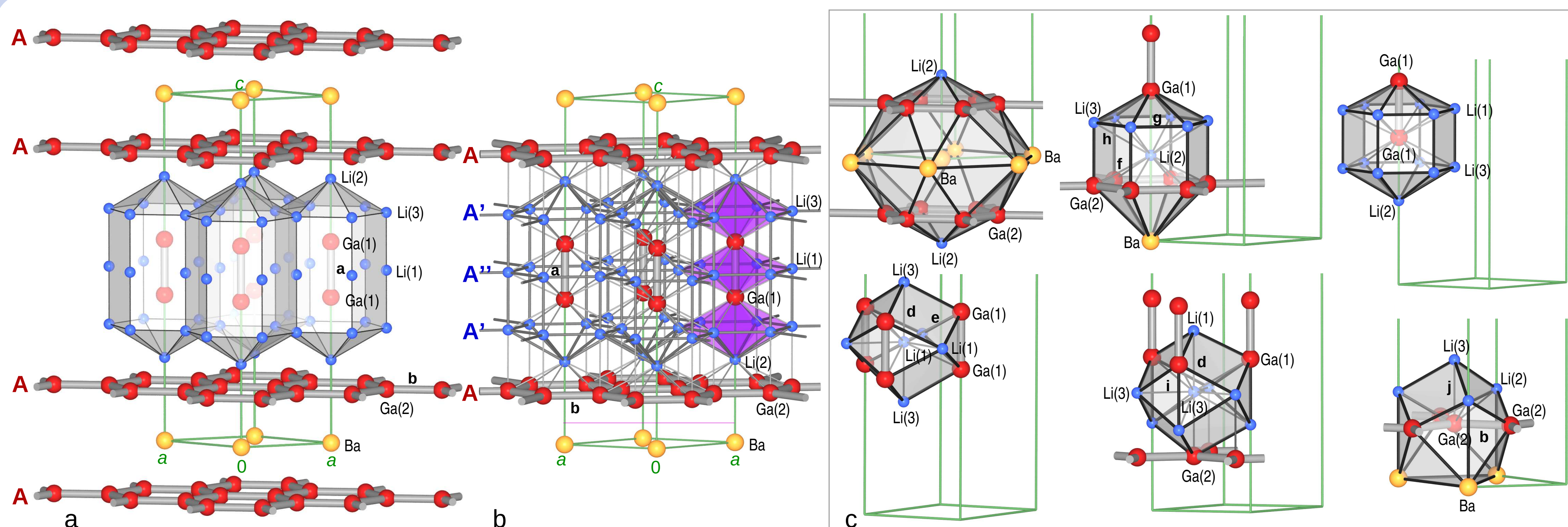


Fig. 3: Unit cell of the crystal structure of BaLi<sub>8</sub>[Ga<sub>2</sub>][Ga<sub>4</sub>] (a,b) and coordination polyhedra of all atoms (c).

The hexagonal structure of the second title phase, BaLi<sub>8</sub>[Ga<sub>2</sub>][Ga<sub>4</sub>] (**C5**, again new structure type, crystal data Table 3 and 4) likewise exhibits [Ga<sub>2</sub>] dumbbell-shaped anions (*d*<sub>Ga(1)–Ga(1)</sub> = 253.3 pm), which are again oriented along the long, in this case hexagonal *c* axis. Here, the overall coordination sphere of these [Ga<sub>2</sub>] unit is an elongated capped hexagonal prism with six extra Li cations

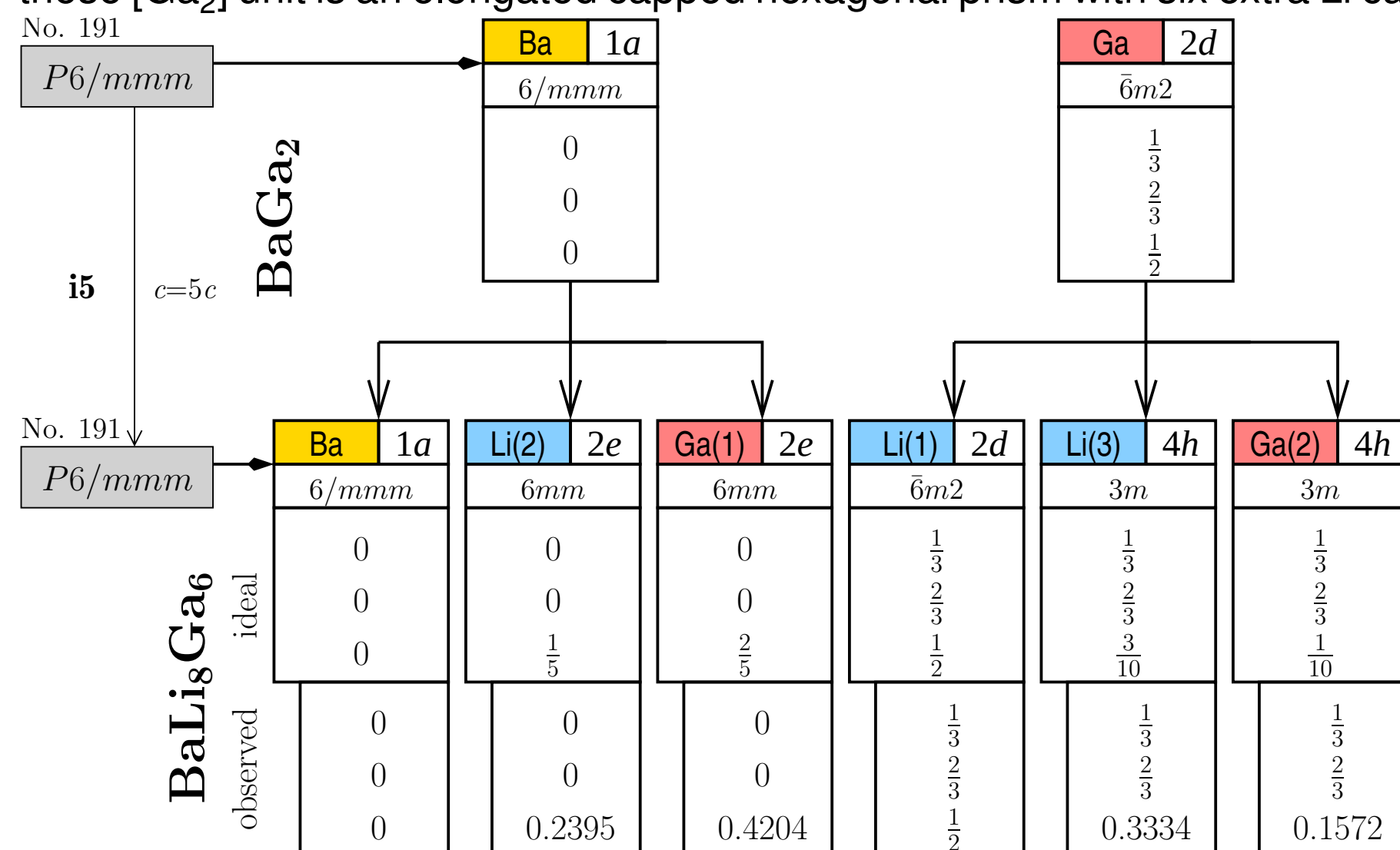


Fig. 4: Group-subgroup tree connecting the structures of BaGa<sub>2</sub> and BaLi<sub>8</sub>[Ga<sub>2</sub>][Ga<sub>4</sub>].

Table 2: Interatomic distances [pm] in the crystal structure of BaLi<sub>8</sub>[Ga(1)<sub>2</sub>][Ga(2)<sub>4</sub>].

| Atoms | Distance | Mult.    | Lbl. | CN       | Atoms | Distance | Mult.    | Lbl. | CN      |
|-------|----------|----------|------|----------|-------|----------|----------|------|---------|
| Ba    | - Ga(2)  | 357.3(1) | 12×  |          | Li(1) | - Li(1)  | 255.2(1) | 3×   | c       |
|       | - Li(2)  | 380.8(2) | 2×   |          |       | - Li(3)  | 265(1)   | 2×   | d       |
|       | - Ba     | 442.0(1) | 6×   |          |       | - Ga(1)  | 284.9(1) | 6×   | e       |
|       |          |          |      | 12+2+6   |       |          |          |      | 6+(5+0) |
| Li(2) | - Ga(2)  | 286.7(5) | 6×   | f        | Li(3) | - Li(3)  | 255.2(1) | 3×   | i       |
|       | - Ga(1)  | 287.7(2) |      | g        |       | - Li(1)  | 264.9(1) |      | d       |
|       | - Li(3)  | 296(1)   | 6×   | h        |       | - Ga(2)  | 280(1)   |      | j       |
|       | - Ba     | 380.8(2) |      | 7+(6+1)  |       | - Ga(1)  | 290.2(7) | 3×   | k       |
|       |          |          |      |          |       | - Li(2)  | 295.7(1) | 3×   | h       |
|       |          |          |      |          |       |          |          |      | 4+(7+0) |
| Ga(1) | - Ga(1)  | 253.3(1) |      | a        | Ga(2) | - Ga(2)  | 255.2(1) | 3×   | b       |
|       | - Li(1)  | 284.9(1) | 6×   | e        |       | - Li(3)  | 280(1)   |      | j       |
|       | - Li(2)  | 287.7(2) |      | f        |       | - Li(2)  | 286.7(5) | 3×   | f       |
|       | - Li(3)  | 290.2(7) | 6×   | k        |       | - Ba     | 357.3(1) | 3×   |         |
|       |          |          |      | 1+(13+0) |       |          |          |      | 3+(4+3) |

centering the long edges of the prism (gray polyhedra [(Ga<sub>2</sub>)@Li<sub>2</sub>]<sub>6</sub> in Fig. 3a). The blocks of [Ga<sub>2</sub>] dumbbells around *z*=1/2 alter with BaGa<sub>2</sub>-like (AlB<sub>2</sub>-type, *d*<sub>Ga(2)–Ga(2)</sub> = 255.2 pm) blocks of identically oriented planar graphite-like nets (around *z*=0). Therewith, the Ba ccps are hexagonal prisms of Ga(2) capped by two Li(2) cations. The six Ba neighbours complete the coordination number to 20 (Fig. 3c). Similar to Ga(2), Li(1) as well as Li(3) also form graphite-analogous 6<sup>3</sup> layers among each other, so that the overall structure can alternatively be described as an isomorphic (i5) symmetry reduced derivative of Ba[Ga<sub>2</sub>], BaLi(2)<sub>2</sub>Ga(1)<sub>2</sub>Li(1,3)<sub>6</sub>Ga(2)<sub>4</sub> (cf. Fig. 4).

### References

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### Experimental

Both Ba/Li gallides were obtained from melts of the elements in ratios SN depicted in Figure 1. The samples, enclosed in Ta crucibles, were heated with a rate of 200 °C/h to 1100 °C and were cooled with slow ramp rates between 10 and 20 °C/h to 300 °C and finally with a high rate to r.t. The phase compositions (cf. arrows in Fig. 1) were checked using powder data.

The crystal structures of the title compounds were determined [7] and refined [8] by means of single crystal X-ray diffraction data (cf. Table 3 and 4).

DFT calculations of the electronic structures of the title compounds and BaGa<sub>2</sub> were performed using the FP-APW+lo method (program WIEN2K, PBE-GGA functional [9]).

### Crystallographic data

Table 3: Crystallographic data of the title compounds.

| Compound                                                                    | Ba <sub>2</sub> Li <sub>2</sub> [Ga <sub>2</sub> ] | BaLi <sub>8</sub> [Ga <sub>2</sub> ][Ga <sub>4</sub> ] |
|-----------------------------------------------------------------------------|----------------------------------------------------|--------------------------------------------------------|
| Crystal system, PEARSON symbol, Z                                           | tetragonal, I12, 2                                 | hexagonal, hP15                                        |
| Space group                                                                 | I4/mmm, no. 139                                    | P6/mmm, no. 191, 1                                     |
| CCDC number                                                                 | 2532325                                            | 2532325                                                |
| Lattice parameters, pm                                                      | a 489.93(6)<br>c 1467.1(2)                         | a 441.970(10)<br>c 1590.34(4)                          |
| Volume of the u.c., 10 <sup>3</sup> pm <sup>3</sup>                         | 352.2(1)                                           | 269.03(1)                                              |
| Density (X-ray), gcm <sup>−3</sup>                                          | 4.036                                              | 3.772                                                  |
| Diffractometer                                                              | Brucker AXS CCD, Mo-Kα radiation                   |                                                        |
| Absorption coefficient μ <sub>Mo-Kα</sub> , mm <sup>−1</sup>                | 18.46                                              | 18.31                                                  |
| θ range, deg.                                                               | 2.8–37.4                                           | 1.3–32.4                                               |
| No. of reflections collected                                                | 4937                                               | 9457                                                   |
| No. of independent reflections                                              | 315                                                | 266                                                    |
| R <sub>int</sub>                                                            | 0.0182                                             | 0.0292                                                 |
| Corrections                                                                 | Lorentz, polarisation, absorption                  |                                                        |
| Structure solution                                                          | Direct Methods, SHELXS-2013 [7]                    |                                                        |
| Structure refinement                                                        | Full-matrix L.S., SHELXL-2019 [8]                  |                                                        |
| No. of free parameter                                                       | 9                                                  | 15                                                     |
| Goodness-of-fit on F <sup>2</sup>                                           | 1.219                                              | 1.196                                                  |
| R values [for reflections with I > 2σ(I)]                                   | R1 0.0194<br>wR2 0.0567                            | R1 0.0179<br>wR2 0.0485                                |
| R values (all data)                                                         | R1 0.0196<br>wR2 0.0569                            | R1 0.0179<br>wR2 0.0485                                |
| Residual elect. density, e <sup>−</sup> × 10 <sup>−6</sup> pm <sup>−3</sup> | +4.1/−1.6                                          | +1.2/−0.9                                              |

Table 4: Atom parameters of Ba<sub>2</sub>Li<sub>2</sub>[Ga<sub>2</sub>] (top) and BaLi<sub>8</sub>[Ga<sub>2</sub>][Ga<sub>4</sub>] (bottom).

| Atom  | Wyckoff position | Atomic coordinates x y z | U <sub>eq</sub> [pm <sup>2</sup> ] | Calculated BADER values charge V <sub>BB</sub> [10 <sup>−6</sup> pm <sup>−3</sup> ] |
|-------|------------------|--------------------------|------------------------------------|-------------------------------------------------------------------------------------|
| Ba    | 4e               | 0 0 0.32621(2)           | 207.4(12)                          | +0.91 36.8                                                                          |
| Li    | 4c               | 0 1/2 0                  | 280(20)                            | +0.81 4.6                                                                           |
| Ga    | 4e               | 0 0 0.08819(4)           | 182.1(14)                          | −1.72 46.5                                                                          |
| Ba    | 1a               | 0 0 0                    | 112(2)                             | +1.08 30.2                                                                          |
| Li(1) | 2d               | 1/3 2/3 1/2              | 119(19)                            | +0.81 3.9                                                                           |
| Li(2) | 2e               | 0 0 0.2395(7)            | 160(20)                            | +0.83 4.0                                                                           |
| Li(3) | 4h               | 1/3 2/3 0.3334(9)        | 520(40)                            | +0.81 4.3                                                                           |
| Ga(1) | 2e               | 0 0 0.42038(4)           | 153(2)                             | −2.16 44.3                                                                          |
| Ga(2) | 4h               | 1/3 2/3 0.15723(3)       | 128(2)                             | −0.84 29.3                                                                          |

### Chemical bonding

The calculated electronic structure of Ba<sub>2</sub>Li<sub>2</sub>[Ga<sub>2</sub>] exhibits a pronounced pseudo-band gap (Fig. 5a). Thus, the compound can be described as an electron-precise ZINTL phase containing [Ga<sub>2</sub>]<sup>6−</sup> anions with a Ga–Ga double bond. BaLi<sub>8</sub>[Ga<sub>2</sub>][Ga<sub>4</sub>] is (chemically, not crystallographically) a stacking derivative of BaGa<sub>2</sub> [5] and the unknown gallide 'Li<sub>6</sub>[Ga<sub>2</sub>]'. In accordance, it's bandstructure (and DOS) is simply an 'overlay' of those of Ba<sub>2</sub>Li<sub>2</sub>[Ga<sub>2</sub>] and BaGa<sub>2</sub> (Fig. 5b and 5c). Similar to BaGa<sub>2</sub> itself, this compound exhibits no (pseudo)-band gap, due to the well-known special features of the bandstructure of AlB<sub>2</sub>-type compounds [6].

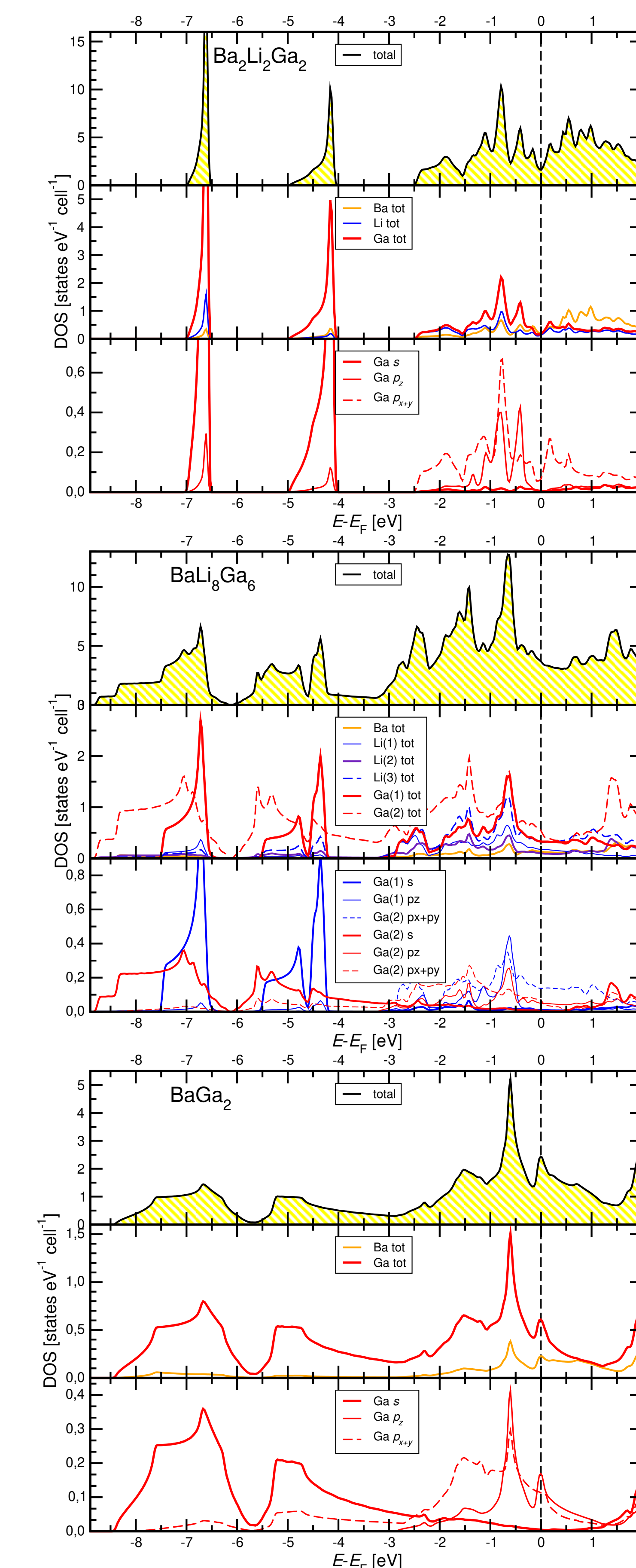


Fig. 5: Comparison of the tDOS/Ga-pDOS of the title compounds with BaGa<sub>2</sub>.

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