



**Figure 1:** The four- (black), five- (white) and six- (grey) connected  $(4^4.6^2)(4^2.6^{10}.8^3)$ -**saab** net while **2** demonstrates the five- and three-connected  $(6^3)(6^{10})$ -**kdd** net<sup>2</sup>.

Two MOFs were prepared from zinc(II) sulphate and 1,3,5-benzenetricarboxylic acid (H<sub>3</sub>BTRI) using the same method although the concentration of starting materials in the solvent system was varied.  $[\text{Zn}_6(\mu_3\text{-(OH)}_2(\text{BTRI})_4(\text{DMF})_{2.5}(\text{H}_2\text{O})_2)] \cdot [\text{Zn}(\text{H}_2\text{O})_3(\text{DMF})_3] \cdot 3 \cdot \text{H}_2\text{O}$  [**1**] and  $[\text{Zn}_2(\text{HBTRI})(\text{BTRI})(\text{H}_2\text{O})_3] \cdot \text{DMA} \cdot 3\text{H}_2\text{O}$  [**2**] are both anionic networks. The counter ions are located in channels in the structure. Scanning electron microscopy (SEM) reveals that **2** “self-heals” upon dehydration and rehydration. **1** demonstrates the six- and three-connected  $(4.6^2)(4^2.6^{10}.8^3)$ -**saab** net while **2** demonstrates the five- and three-connected  $(6^3)(6^{10})$ -**kdd** net<sup>2</sup>.

Topological analysis allows for a simple comparison between different MOFs.

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### Structural characterization of LaTi<sub>2</sub>Al<sub>9</sub>O<sub>19</sub>

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LaTi<sub>2</sub>Al<sub>9</sub>O<sub>19</sub> [1] was prepared as single phase ceramics that was structurally characterized by means of laboratory X-ray powder diffraction. The compound was found to be isostructural with SrTi<sub>3</sub>Al<sub>8</sub>O<sub>19</sub> [2] and it crystallizes in monoclinic *C2/c* space group with the following unit cell parameters:  $a=22.59355(18)$  Å,  $b=10.99919(9)$  Å,  $c=9.72968(7)$  Å,  $\beta=98.5634(5)^\circ$ ,  $V=2390.97(3)$  Å<sup>3</sup>,  $Z=8$ .

The fundamental building units are AlO<sub>6</sub>- and TiO<sub>6</sub>-octahedra which are interconnected by AlO<sub>4</sub>-tetrahedra and La<sup>3+</sup> ions into a complex network. Most simply, the structure can be represented as a system of close-packed octahedral layers of three types, i. e. layers A, B and C. In each unit cell, ten of these layers stack along *a* edge in a sequence ABCCBABCCBA. Typical fragments for layer A are pairs of edge-sharing AlO<sub>6</sub>-octahedra which are further connected *via* vertices to La<sup>3+</sup> ions and AlO<sub>4</sub>-tetrahedra, respectively. Typical fragments of layers B and C are (TiAl<sub>5</sub>Ti)O<sub>28</sub> hook-like groups of edge-sharing octahedra; the main difference between B and C layers is that B layers additionally include La<sup>3+</sup> ions while C layers consist of AlO<sub>4</sub>-tetrahedra. Layers of octahedra are linked *via* edge- and vertex- sharing between A-B and

C-C layers whereas the connections between B and C layers run only through the sharing of vertices. Neither within the layers nor between them there are any face-sharing octahedra and AlO<sub>4</sub>-tetrahedra connect with the other fragments only through vertices. With the described packing of the layers and their connections, the 12-fold coordination of lanthanum ions is achieved. The plausibility of the obtained structure was confirmed by bond valence sums and global instability index calculations.

The initial pattern matching shows resemblance between LaTi<sub>2</sub>Al<sub>9</sub>O<sub>19</sub> and one of the largest structures determined *ab initio* from powder data, La<sub>3</sub>Ti<sub>5</sub>Al<sub>15</sub>O<sub>37</sub> [3]. In our opinion, the latter is not completely physically and chemically reasonable as it contains compositional as well as structural inconsistencies (e. g. some metal-metal distances are too short) that result in significant discrepancies of bond valence sums from the nominal atomic valences and high value of global instability index of 0.65 valence units.

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### Composition-dependent negative thermal expansion in tetracyanidoborate materials

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Coordination framework materials are extended crystalline networks composed of repeating units of metal ions and bridging ligands. As virtually limitless combinations of metal ions, ligands and structures are possible, these materials can display a wide variety of different properties, including porosity, catalysis, gas storage, magnetic behaviour, and negative thermal expansion [1]. This research expands the current literature on the properties of cyanide (C≡N<sup>-</sup>) bridged framework materials by presenting the first negative thermal expansion results for a series of isostructural materials containing the tetracyanidoborate anion, [B(CN)<sub>4</sub>]<sup>-</sup>, with a range of *s*- and *d*-block metal ions (Li<sup>+</sup>, Na<sup>+</sup>, Cu<sup>+</sup> and Ag<sup>+</sup>).

Negative thermal expansion (NTE) describes the tendency of a material to shrink reversibly upon heating and has been demonstrated in a number of cyanide-bridged framework materials to date, including the compounds Zn(CN)<sub>2</sub> and Cd(CN)<sub>2</sub>, [2] which are each isostructural with the materials in this study. Cooperative transverse vibrations (phonon modes) are responsible for the overall contraction of materials in this class,[3] and this work contributes to a greater understanding of the influence of framework flexibility on observed NTE by studying the effects of systematically changing the metal ion in otherwise identical structures. Results to date from synchrotron powder X-ray diffraction, neutron powder diffraction and single crystal X-ray diffraction indicate that two of these compounds, Na[B(CN)<sub>4</sub>] and Ag[B(CN)<sub>4</sub>], undergo amongst the largest isotropic NTE currently known ( $\alpha = -31 \times 10^{-6}$  K<sup>-1</sup> and  $-25 \times 10^{-6}$  K<sup>-1</sup> at 100 K, respectively;  $\alpha = \delta l / l \cdot \delta T$ , where *l* is the cubic unit cell dimension) [4]. The magnitude of transverse vibrations and thus NTE in these compounds appears strongly correlated with the strength and flexibility of the metal-ligand interactions and the degree of proximity of the two interpenetrated nets that comprise the structures.