



Figure 1: The four- (black), five- (white) and six- (grey) connected $(4^4.6^2)(4^6.6^4)(4^8.6^6.8)$ network of **3**

Two MOFs were prepared from zinc(II) sulphate and 1,3,5-benzenetricarboxylic acid (H_3BTRI) using the same method although the concentration of starting materials in the solvent system was varied. $[Zn_6(\mu_3-(OH)_2(BTRI)_4(DMF)_2.5(H_2O)_2)] \cdot [Zn(H_2O)_3(DMF)_3] \cdot 3 \cdot 1H_2O$ [**1**] and $[Zn_2(HBTRI)(BTRI)(H_2O)_3] \cdot DMA \cdot 3H_2O$ [**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 $(4.6^2)(4^2.6^{10}.8^3)$ -**sab** net while **2** demonstrates the five- and three-connected $(6^3)(6^{10})$ -**kdd** net².

Topological analysis allows for a simple comparison between different MOFs.

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Structural characterization of $LaTi_2Al_9O_{19}$

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$LaTi_2Al_9O_{19}$ [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 $SrTi_3Al_8O_{19}$ [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, $\beta=98.5634(5)^\circ$, $V=2390.97(3)$ Å³, $Z=8$.

The fundamental building units are AlO_6 - and TiO_6 -octahedra which are interconnected by AlO_4 -tetrahedra and La^{3+} 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 ABCBABCBA. Typical fragments for layer A are pairs of edge-sharing AlO_6 -octahedra which are further connected *via* vertices to La^{3+} ions and AlO_4 -tetrahedra, respectively. Typical fragments of layers B and C are $(TiAl_5Ti)O_{28}$ hook-like groups of edge-sharing octahedra; the main difference between B and C layers is that B layers additionally include La^{3+} ions while C layers consist of AlO_4 -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_4 -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 $LaTi_2Al_9O_{19}$ and one of the largest structures determined *ab initio* from powder data, $La_3Ti_5Al_{15}O_{37}$ [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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Keywords: rietveld refinement, XRPD, $LaTi_2Al_9O_{19}$

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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 ($C\equiv N$) bridged framework materials by presenting the first negative thermal expansion results for a series of isostructural materials containing the tetracyanidoborate anion, $[B(CN)_4]^-$, with a range of s - and d -block metal ions (Li^+ , Na^+ , Cu^+ and Ag^+).

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 $Zn(CN)_2$ and $Cd(CN)_2$, [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, $Na[B(CN)_4]$ and $Ag[B(CN)_4]$, undergo amongst the largest isotropic NTE currently known ($\alpha = -31 \times 10^{-6} K^{-1}$ and $-25 \times 10^{-6} K^{-1}$ 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.

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Surface modification of hydroxyapatite by grafting alkyl phosphonic dichloride

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The inorganic-organic hybrids have interesting applications resulting from the combination of some characteristic properties of the inorganic substrate (mechanical and chemical properties, exchange capacity, bioreactivity, optical properties...) with those of the organic grafting (polymerizability, superficial tension...). Such modified materials are used in catalysis, chromatography, biomedical domain...

A suspension of calcium hydroxyapatite $\text{Ca}_{10}(\text{PO}_4)(\text{OH})_2$ was treated by the different alkylphosphonates (R-POCl_2 , R= methyl or octyl) in organic solvent using a molar ratio $x=2$ or 4 , $x=n(\text{organic})/n(\text{apatite})$. The surface of the modified CaHAp was characterized using X-ray diffraction, IR and ^{31}P MAS-NMR spectroscopies, chemical analysis and Atomic Force Microscopy (AFM). No remarkable change in XRD patterns was observed after grafting. FTIR results indicated that new vibration modes related to phosphonate groups appear essentially at 2930, 1315, 945, 764 and 514 cm^{-1} . The ^{31}P MAS-NMR spectra of treated hydroxyapatite show new signals due to the formation of organic-inorganic bonds in the surface between the superficial hydroxyl groups of the apatite ($\equiv\text{CaOH}$ and $\equiv\text{POH}$) and alkyl phosphonic dichloride. AFM proved that the texture surface was changed and roughness decreased. The number of phosphonate groups grafted, in the modified materials, was calculated from chemical analysis results.

Keywords: apatite, functional, AFM

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An *ab initio* study of ZrO_2 - HfO_2 solid solution with cotunnite structure

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Previous experimental and theoretical studies [1], [2], [3], [4] suggested that cotunnite-type zirconia and hafnia, as well as their solid solutions, could be candidates for superhard materials due to their high bulk moduli. Another possible application of cotunnite-type ZrO_2 and HfO_2 as waveguide materials is discussed here. An investigation of these questions requires knowledge of the elastic stiffness tensor as a function of chemical composition. According to the results of *ab initio* calculations [2, 4 and this study] the elastic stiffness coefficients of the HfO_2 polymorphs are significantly larger than those of the corresponding ZrO_2 polymorphs, while the volumes of the ZrO_2

polymorphs are consistently smaller. It is not obvious whether the contraction of the HfO_2 structure due to the incorporation of a smaller, but more compressible cation causes an increase in the bulk modulus, or how the incorporation of the larger, but less compressible Hf cation changes the elastic stiffness properties of ZrO_2 .

We have computed the elastic stiffness tensors of ZrO_2 and HfO_2 polymorphs with baddeleyite-type ($P2_1c$), $Pbca$ and cotunnite-type ($Pnma$) structures in order to obtain the anisotropy of sound wave phase velocities and have calculated the thermodynamic mixing properties of HfO_2 - ZrO_2 solid solutions with the cotunnite structure. The calculations were based on density functional theory within the generalized gradient approximation (GGA) with PBE and PBEsol functionals [5, 6]. The calculations were carried out with the program CASTEP [7] using high-performance computers at the University of Frankfurt and at the Moscow State University.

The anisotropic sound wave phase velocities were determined using the Christoffel tensor [8]. Despite the lower stiffness, the calculated speeds of sound wave propagation are generally higher for ZrO_2 polymorphs because of their lower density. Cotunnite-type ZrO_2 has rather high longitudinal acoustic wave velocities (about 8 km/s) which are not strongly dependent on direction and thus could be considered for applications as a solid acoustic waveguide material.

The solid solution is characterized by unusual negative enthalpy and volume of mixing. The ordering energies corresponding to the reaction $\text{ZrZr} + \text{HfHf} = 2\text{ZrHf}$ were calculated for 9 interatomic distances within a $2 \times 2 \times 1$ supercell. These energies are very small (< 1 kJ/mol). This suggests that any intermediate ordered compound can be used as a probe for the elastic stiffness of the solid solution at intermediate compositions. The calculations of elastic stiffness tensors of ordered compounds within the HfO_2 - ZrO_2 binary are currently underway.

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Crystal structures and ultramicroporosity in Mg & Ca tetrakisphosphate hybrids

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The chemistry of hybrid organic-inorganic materials has experimented, during the past decade, an exponential growth due to the high number of possible applications in many fields such as gas storage, catalysis, and ion exchange [1]. The phosphonate-based metal organic framework are today under investigation, and it is a common opinion that the best results are forthcoming. This is mainly due to the fact that generally the phosphonic acids have a higher flexibility degree, with respect to the carboxylic ligands, leading to a major structural variability and therefore to a lower control in their design