

pressure-cell was loaded into a helium flow cryostat.

Analysis of the recorded data shows that $\text{Fe}_{1.087}\text{Te}$ is tetragonal with space group $P4/nmm$ at 80 K and ≈ 0.45 GPa. A commensurate antiferromagnetic monoclinic phase with propagation vector $\mathbf{k} = (\frac{1}{2} 0 \frac{1}{2})$ was observed at ≈ 2 K and 0.44 GPa. The magnetic moments of iron of 1.74(7) BM were found to be parallel with the b -axis. The magnetic structure observed at ≈ 2 K and 0.44 GPa is closely related to the magnetic structure observed at ambient pressure and $T < 63$ K but with a reduced magnetic moment of iron [1]. The tetragonal $P4/nmm$ structure was preserved at a pressure of 1.15 GPa and 80 K. Cooling at this pressure revealed the existence of a new magnetic phase between ≈ 60 and ≈ 48 K. The analysis of data recorded at 55 K shows that the magnetic phase is incommensurate with propagation vector $\mathbf{k} = (0.445 0 \frac{1}{2})$, while the chemical structure was found to be orthorhombic, space group $Pmmn$. The data could be fitted with both a sinusoidal (magnetic moments parallel to the b -axis) and a cycloidal (magnetic moments rotating in the a,c -plane) model of the magnetic structure. This magnetic phase seems to be stable between 48 and 60 K. This phase corresponds to the HP1 phase observed by Okada *et al.* by resistivity and magnetization measurements [2]. An incommensurate antiferromagnetic structure with propagation $\mathbf{k} = (0.495, 0, 0.486)$ was observed at ≈ 2 K and 1.15 GPa. The observed magnetic structure is closely related to the commensurate antiferromagnetic structure observed at ≈ 2 K and 0.44 GPa but with a sinusoidal modulation with an amplitude of 1.98(8) BM and it develops gradually upon cooling from 48 to 2 K.

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Keywords: magnetic structure, neutron diffraction, high-pressure.

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Magnetic ionic liquids 1-ethyl- and 1-butyl-3-methylimidazolium tetrachloroferrate(III). Crystallization monitored by powder x-ray thermodiffraction

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Ionic Liquids (ILs) are salts with melting points below 100°C, i.e. they are liquids comprised entirely of cations and anions. ILs exhibit a unique set of physical properties that make them interesting for different applications: non-volatility, high thermal stability, wide liquid-state temperature range, good solvents for synthesis, etc. [1]. In addition, ILs containing transition metal complexes show very interesting magnetic properties [2]. It is known that the physicochemical properties of the ILs can be tailored by the selection of both cation and anion components, but the origins of their unique behavior are still relatively poorly understood [3]. Previous studies demonstrate that a correlation exists between the structure of the ILs in the solid and liquid states. Therefore the elucidation of the crystal structures of these compounds would provide a strong basis from which the ILs properties can be further rationalized. ILs display very complicated thermal and crystallization behavior, such as supercooling and glass formation, pre-melting or solid-solid phase transitions [4]. Usually, ILs thermal behavior studies have been performed by differential

scanning calorimetry but, to our knowledge, no thermodiffraction studies have been reported yet.

One of the most prominent cation-type is the N-N'-dialkylimidazolium. Their counterion may range from a simple halide to more sophisticated anions. We have investigated the thermal behavior of the magnetic room temperature ionic liquids (MRTL) 1-ethyl-3-methylimidazolium tetrachloroferrate(III), EMIM[FeCl₄], and 1-butyl-3-methylimidazolium tetrachloroferrate(III), BMIM[FeCl₄], by using X-ray powder thermodiffraction and differential scanning calorimetry. EMIM[FeCl₄] displays thermal polymorphism and exhibits reversible and irreversible solid-solid crystalline transitions with the formation of metastable phases. On the other side, for BMIM[FeCl₄] homogeneous crystallization from the melt is inhibited and glass formation occurs on cooling. This amorphous solid crystallizes below room temperature by devitrification on heating from the cooled glassy state. Both systems show a very complex behavior with formation of metastable phases depending on the materials thermal histories.

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Dynamic and crystallographic neutron studies of $\text{La}_{1-x}\text{Ba}_{1+x}\text{GaO}_{4-2x}$: toward a better understanding of the proton diffusion in new fuel cell materials

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Fuel cells convert chemical energy directly to electrical energy cleanly and efficiently. A crucial part of a fuel cell is the electrolyte, a material that conducts ions. On the way towards practicable solutions, one of the biggest problems at the moment is the lack of stable and effective ionic conductor at the desired intermediate temperature range (100–600°C). Solid oxide proton conductors present many advantages compared to the other candidates as they offer higher efficiency than conventional oxygen ion materials.

Novel oxide structures such as $\text{La}_{1-x}\text{Ba}_{1+x}\text{GaO}_{4-2x}$ containing tetrahedral units and high proton and oxide ion conductivities have been shown to be potential candidates at intermediate temperatures ionic conductors [2,3]. Proton conductivity dominates in wet atmospheres below 700 °C, giving rise to as high protonic conductivity as 10^{-4} S cm^{-1} at 500°C [3,4]. In these systems water can be incorporated into the structure as protonic defects from humid atmospheres. However, despite the importance of proton conduction for energy applications, our understanding of the complex mechanisms driving the proton transport is still not well understood [1].

High-resolution neutron powder diffraction as well as quasi-elastic measurements will be presented to highlight our knowledge of the migration/diffusion of protons into the material and therefore understand the dynamic of the phenomenon.

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The tale of molecule vi: a benchmark sulfonimide in crystal structure prediction

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Many compounds can crystallize into more than one unique crystal structure, a well documented phenomenon known as polymorphism. [1] There can be significant variations in physical properties between the polymorphs of a compound. [2] Crystal structure prediction (CSP) makes an important contribution to understand polymorphism, to help exploit its opportunities and to help avoid potential problems. To assess the progress in CSP technologies, a series of Blind Tests has been organized by the Cambridge Crystallographic Data Centre.

Molecule VI (see Figure 1) was one of the target compounds in the 2001 Blind Test. [3] No participant predicted the then only known experimental polymorph (form I). Two additional polymorphs, forms II and III, were later discovered. [4], [5] It was concluded that CSP failed because these calculations tend to focus on the thermodynamically most stable structures, whilst the Molecule VI polymorphs may be kinetically favored. [4], [5] It further led to a comment on "structure prediction, which would be most valuable for process chemistry, has still a way to go". [6]

To investigate fully the polymorphism of Molecule VI, a CSP was conducted using the GRACE software, [7] which correctly predicted the structures of all four target compounds in the 2007 Blind Test. [8] In the current study, the rank 1, 2 and 3 predictions were in good geometric agreements with the forms I, III and II experimental structures of Molecule VI respectively. [9] The relative stabilities of these predicted polymorphs were consistent with differential scanning calorimetry results. [5]

In conclusion, it is feasible to predict the crystal structures of small organic molecules by considering crystallization thermodynamics only, provided that the accuracy of the lattice energy calculation method used is sufficient. Yet, it is not possible to predict the outcome of a specific crystallization experiment, because it would be beyond current computational capabilities to consider all relevant kinetic effects on the crystallization process.

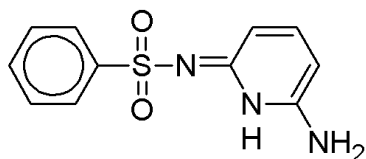


Figure 1 The molecular structure of molecule VI

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Hybrid evolutionary approach for material design: search for superhard materials

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We have developed a method for prediction of the hardest crystal structures in a given chemical system. It is based on the evolutionary algorithm USPEX and involves the concept of *hybrid global optimization*, where global optimization with respect to a desired property (hardness) is conducted in the space of local minima of the (free) energy. To calculate the hardness of a crystal, we employed the electronegativity-based hardness model [1] which we have augmented with bond valence model and multi-color graph theory. These extensions enable correct description of the hardness of layered, molecular and low-symmetry crystal structures.

Applying our method to C and TiO₂, we have (i) obtained a number of low-energy carbon structures with hardness slightly lower than diamond and (ii) proved that TiO₂ in any of its possible polymorphs cannot be the hardest oxide, its hardness being below 17 GPa, thus resolving a long-standing controversy.

The same concept of hybrid global optimization can be used for optimizing other properties of materials.

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Crystal energy landscapes of intrinsically porous molecules

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Nanoporous materials have potential applications in heterogeneous catalysis, gas storage and separation. While this research area has been dominated by nanoporous network materials such as metal-organic frameworks (MOFs), significant recent attention has been given to the preparation of nanoporous solids from synthetically pre-organized molecular pores [1]. These molecular materials offer advantages such as solution processability and controlled modular assembly of chemically distinct pores *via* crystallization. A major obstacle which has limited the rational design of molecular porous materials is the challenge of predicting the assembly of molecular crystals.