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Hematopoietic prostaglandin(PG) D synthase(H-PGDS) is responsible for production of PGD₂ as an allergic or inflammatory mediator in mast cells and Th2 cells[1].

We solved the crystal structure of human H-PGDS bound to the cofactor glutathione(GSH) and HQL-79, a novel inhibitor of H-PGDS in the presence of Ca²⁺ or Mg²⁺, showing the HQL-79 molecule penetrated into the active site between Trp104 and GSH binding site with its biphenyl rings locating at the bottom of the active site, inducing the conformational change of Trp104 with a 60 degree rotation and a 3.7 Å movement of the indole ring.

The surface plasmon resonance analysis revealed that the binding affinity (KD) of HQL-79 is accelerated 10-fold in the presence of both Mg²⁺ and GSH, revealing that the GSH molecule strongly bound in the Mg²⁺-bound form helped the insertion of the HQL-79 molecule, reducing the *Ki* value to be 5 μM with 10-fold in the presence of Mg²⁺. HQL-79 specifically inhibits H-PGDS activities competitive to the substrate PGH₂, and non-competitive to the cofactor GSH[2].

[1] Urade Y., Hayaishi. O., *Vitam Horm*, 2000, **58**, 89-120. [2] Aritake K., et.al., *submitted*.

Keywords: prostaglandins, anti-inflammatory compounds, X-ray structural analysis

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Polymorphism and Photochromism of Salicylideneaniline

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Organic compounds exhibiting photo- or thermochromicity have been of considerable interests owing to their properties and possible applications. The photochromism of salicylideneaniline (SA) was discovered by Senier *et al.* at the beginning of last century. In 1964, Cohen *et al.* [1] observed polymorphism.

It is generally accepted that the stable form of SA in the ground state is the enol form, with an intramolecular hydrogen bond between the hydroxyl group and the nitrogen atom. Upon photoexcitation of this enol form with UV light, it undergoes an ultrafast proton transfer from the hydroxyl group to the nitrogen, due to the electronic redistribution in the excited state. The proton transfer generates a keto tautomer in the excited singlet state.

Here, we report on the alpha-2-polymorph structure of SA in the ground state [2], already mentioned by Cohen. We shall also described a new polymorph, beta, which features a planar SA molecule and is therefore thermochromic. Then, we revisit the alpha-1-polymorph structure of SA described by Destro *et al.* [3], but reconsidering their hypothesis. We suggest a lowering of the symmetry with the aim to improve the structure solution.

[1] Cohen M.D., Schmidt G.M.J., Flavian S., *J. Chem. Soc.*, 1964, 2041-2051. [2] Arod F., Gardon M., Pattison P., Chapuis G., *Acta Cryst.*, 2005, *in press*. [3] Destro R., Gavezzotti A., Simonetta M., *Acta Cryst.*, 1978, **B34**, 2867-2869.

Keywords: photochromism, polymorphic structures, properties and structure relationships

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Structure, Chemical Bonding and Thermoelectric Performance of Zn₄Sb₃

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Thermoelectricity is due to play an important role in today's energy challenges. The ideal thermoelectric material is a *phonon glass*

and electron crystal, i.e. has a low thermal conductivity combined with high electrical conductivity and Seebeck coefficient. Zinc-antimonide, with formal stoichiometry Zn₄Sb₃, nicely fulfills these requirements, but to explain its unusual combination of properties was not possible because its detailed structure remained for a long time unknown. Now, a crystal structure consistent with the observed mass density has been proposed for the first time by structurally refining single-crystal XRD data, and by analysing powder-synchrotron-radiation diffraction data with a Rietveld-MEM technique.[1,2] Zn₄Sb₃ has a regular Sb lattice, while Zn is distributed over several non-equivalent sites with fractional occupancy. To deconvolute the space-time average inherent to XRD we carried out an extensive computational investigation, and we identified the atomistic arrangements through which the system evolves.[2] In this poster, the bonding and atomic properties of these structures are investigated within the formalism of the Quantum Theory of Atoms In Molecules, and contrasted to the proposed Zintl-phase description of Zn₄Sb₃. [1,2] Furthermore, band-structure calculations of the electronic transport properties are performed to unravel how the atomic structure relates to the material's thermoelectric performance.

[1] Snyder G.J., Christensen M., Nishibori E., Caillat T., Iversen B.B., *Nature Mater.*, 2004, **3**, 458. [2] Cargnoni F., Nishibori E., Rabiller P., Bertini L., Snyder G.J., Christensen M., Gatti C., Iversen B.B., *Chem. Eur. J.*, 2004, **10**, 3861.

Keywords: XRD, ab-initio computations, thermoelectricity

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Synthetic Chrysotile: Effect of Foreign Ions on the Hydrothermal Synthesis

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Conventional and synchrotron radiation X-ray diffraction have been used to characterize chrysotile nano-crystals synthesized under bland hydrothermal conditions. In particular, the effects on the crystallization kinetics of the presence of Al, Fe and Ti species have been evaluated.

Studies were conducted both *in situ* using synchrotron radiation X-ray diffraction at the Daresbury Laboratory station 16.4 and *ex situ* on the material synthesized in a Parr 4652 laboratory reactor.

The synthesis of the material was obtained under conditions usually considered very bland to form complex silicates.

Chemical physical, structural and morphological characterization of the synthesized crystals allowed to know the role of the foreign ions on the observed materials features.

Keywords: nanotubes, chrysotile, hydrothermal synthesis

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Structural Comparisons of Three Intermetallic Antimonide Families

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High quality single crystals of the ternary antimonides LnNi₃Sb₂ (Ln = Y, Gd – Er; *x* ≈ 0.6) and LnNiSb₃ (Ln = Pr, Nd, Sm) have been grown from an antimony flux. Their crystal structures have been characterized by single crystal X-ray diffraction experiments. The LnNi₃Sb₂ compounds adopt the HfCuSi₂ structure type and crystallize in the tetragonal space group *P4/nmm* with *Z* = 2 and lattice parameters of *a* ≈ 4.3 Å, *c* ≈ 9.3 Å, and *V* ≈ 170 Å³. These compounds are layered and consist of Ln-capped Sb square nets and Ni tetrahedral frameworks arranged in an anti-PbO fashion. The LnNiSb₃ compounds adopt the CeNiSb₃ structure type and crystallize in the orthorhombic space group, *Pbcm* (No. 57), *Z* = 12, with lattice

parameters $a \approx 12.5$, $b \approx 6.2$, $c \approx 18.4$ Å, and $V \approx 1400$ Å³. Similar to the $LnNiSb_2$ compounds, these compounds are layered but consist of rare-earth atoms located above and below planes of nearly square, buckled Sb nets, however with layers of highly distorted edge- and face-sharing $NiSb_6$ octahedra. The structures of the $LnNi_xSb_2$ ($Ln = Y, Gd - Er$; $x \approx 0.6$) and $LnNiSb_3$ ($Ln = Pr, Nd, Sm$) compounds are similar to the structure of the simple binary phases $LnSb_2$ ($Ln = La-Nd, Sm, Gd-Er$). In an effort to correlate and elucidate the origin of the physical behavior observed, the structural units found within these three families will be compared.

Keywords: rare-earth, antimonides, single crystal

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The Crystal Growth and Structure and Property Relationships of Pr-Ni-Ga Phases

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Single crystals of two new ternary compounds, Pr_2NiGa_{10} and Pr_2NiGa_{12} were synthesized by flux methods. Single crystal X-ray diffraction data were collected and structures were solved for Pr_2NiGa_{10} and Pr_2NiGa_{12} . Pr_2NiGa_{10} , which crystallizes in a tetragonal space group $I4/mmm$, $Z = 2$, with the lattice parameters: $a = 4.2330$ (4) and $c = 26.364$ (3), $R_{\text{factor}} = 2.71\%$, was found to be isostructural to Ce_2PdGa_{10} .^[1] Pr_2NiGa_{12} , which crystallizes in tetragonal space group $P4/nbm$, $Z = 2$, with the lattice parameters: $a = 6.0080$ (7) and $c = 15.454$ (3), $R_{\text{factor}} = 4.2\%$, was found to be isostructural to Ce_2PdGa_{12} .^[2] The structure, transport, and magnetic properties of these compounds will be compared to other Ln_2PdGa_{10} ($Ln = La, Ce$) and Ln_2PdGa_{12} ($Ln = La, Ce$) phases.

[1] Millican J. N., Macaluso R. T., Young D. P., Moldovan M., Chan J. Y., *J. Solid State Chem.*, 2004, 177, 4695-4700. [2] Macaluso R. T., Millican J. N., Lee H., Nakaatsuji S., Carter B., Nelson M., Fisk Z., Chan J.Y., 2005, *in preparation*.

Keywords: Pr-Ni-Ga phases, structural features, physical properties

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Structural Basis for the Diverse DNA Sequence Recognition by C/EBPβ Homodimer

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The CAAT-enhancer binding proteins (C/EBPs) are the bZIP family transcriptional regulatory factors, which play important roles during cell differentiation through regulating various gene expressions.

There are several kinds of the transcription factors belonging to the bZIP family such as c-Jun, Fos, CREB, etc, which recognize their specific DNA sequence as a homodimer or a heterodimer. In the case of a homodimer, the recognition sequences found in the native promoters are usually symmetric.

On the other hand, C/EBPs recognition sequences in the native promoters are mostly asymmetric even when C/EBPs, also belonging to the bZIP family, work as a homodimer, resulting in their much variety of target sequences.

To elucidate molecular mechanisms of C/EBPs for specific DNA recognition, we performed the structural analyses of several kinds of binary complexes composed of C/EBPβ, which is a member of C/EBPs, and various native promoter sequences or an artificial high affinity symmetric sequence, and the functional analyses such as a measurement of DNA binding affinity of C/EBPβ or its mutants designed from the structure using Surface Plasmon Resonance (SPR).

We could identify several conserved amino acids characteristic for C/EBPβ, which would play critical roles in its recognition of asymmetric DNA sequences.

Keywords: protein-DNA recognition, transcription factor, DNA-protein complexes

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Ab-initio Modeling of Electronic Transport Properties: a Structural Informer

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Functional materials often need to be structurally adjusted for optimizing their relevant properties. In the case of a thermoelectric (TE) material, the original atomic composition and structure is modified to enhance its figure of merit $Z \cdot T = T \cdot (S^2 \sigma / \kappa)$, where the Seebeck coefficient S , the electrical and thermal conductivity σ and κ are the material's transport properties. Doping is a common line of attack to optimize a TE material, and the relationship between the possible structural outcomes and the related transport properties, upon doping, may serve as a guidance to rationalize this empirical $Z \cdot T$ improvement procedure.

Recently [1] it has been shown that the *ab-initio* calculated electronic transport (ET) properties are useful *structural informers* for the doped semiconductor crystalline systems since these properties are rather sensitive to the location, the chemical nature and the concentration of the dopant atom. This fact establishes the *ab-initio* modeling as a particularly suited approach to assist the TE materials optimization.

The case of X-doped (X=Te, Sn, Fe, alkaline earth metal) $CoSb_3$ is as an interesting example of the ability of this approach to enlighten the effects the structural modifications have on a potentially highly performing TE material, especially when experiments are unable to recover detailed information on the geometric and electronic structure.

[1] Bertini L., Gatti C., *J. Chem. Phys.*, 2004, 121, 8983.

Keywords: ab-initio calculations, crystal Structure, electronic transport properties

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Crystal Structures and Physical Properties of Flurbiprofen Salts

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Flurbiprofen is a nonsteroidal anti-inflammatory agent bearing a carboxyl group. As the free acid its aqueous solubility is only 0.03 mg mL⁻¹. Hydrophobicity of the counter ion does not fully determine the solubility of its amine salts[1], being 0.37, 2.80, 0.64 and 0.17 mg mL⁻¹ for the cyclohexyl(CH)-, hexyl-, octyl- and adamantyl(AD)-ammonium salts respectively. ΔH of fusion is 159.0 J g⁻¹ for the CH but only 81.0 J g⁻¹ for the hexylammonium salt.

We report structures of the stable CH and AD salts, acquired with synchrotron radiation because they exist as fine needles.

Crystal, T	a/Å	b/Å	c/Å	β/°	ρ/Mgm ⁻³
CH, 150K	14.7991	6.3014	19.7845	91.273	1.237
CH, 291K	15.0841	6.2988	19.8939	91.146	1.207
AD, 150K	39.350	6.3973	16.9976	90	1.228
AD, 291K	39.514	6.4257	17.1454	90	1.213

In both cases the cycloalkyl group covers the 2-fold disordered fluorophenyl ring, forming a clear hydrophobic domain. Hydrogen bonds join three ammonium H atoms to two carboxylate O atoms and create infinite ladders along the short b axis, which in CH shows no thermal expansion while the a axis expands by 1.9% over 141K.

[1] Anderson B.D., Conradi R.A., *J. Pharm. Sci.*, 1985, 74, 815.

Keywords: solubility, thermal expansion, synchrotron radiation