

layer with oxygen and La/Ba atoms is stacked by two types. One is cubic ABCABC stacking for perovskite layer and hexagonal ABAB stacking for junction slabs which is composed three octahedral with face contact. There are three positions for Ba/La ions as follows: *A1* position with La and Ba is located near vacant octahedron, *A2* position is located next stacking layer, and *A3* position is occupied the center of perovskite layer. Structures of BaLa₄Ti₄O₁₅ substituted Ca and Sr for Ba are also analyzed. And relationship between structure and properties of them are presented.

Keywords: microwave dielectrics, homologous compound, hexagonal layered perovskite

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Extraordinary Negative Thermal Expansion in the Smallest Chiral Amino Acid Alanine

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Amino acid construction consists of a carboxylic acid (-COOH) and an amino (-NH₂) functional group attached to the same tetrahedral carbon atom, the α -carbon. Every amino acid, with the exception of glycine, comes in two forms, a left-handed (L) and a right-handed (D) version, which are identical mirror images of each other. However, protein chains cannot be formed from a mixture of D and L.

We report on high resolution X-ray and neutron scattering diffraction as well as quasi-elastic neutron (QENS) studies on crystalline L- and D-alanine over a wide temperature range. Our aim is to verify the possibility predicted by the Nobel Laureate A. Salam, that a phase transition, related to a break of the as C α -H bond, occurs in alanine. While no change in the space group symmetry was observed, a negative thermal expansion, by discrete steps, along the c -axis is observed till the melting point. Additional anomalies are also noticed in the a and b lattice constants at 170K. Moreover, the evolution of the mean-square displacement, obtained from the QENS, data shows a steadily increase on heating, but near 150K and again near 200K a deviation from the expected behavior is observed. The results suggest the excitation of new degrees of freedom, possibly due to a progressive conformational change of the NH₃⁺ group. The ramifications of this study can be extremely interesting for the understanding of homochirality as well as a breakthrough in molecular mapping via non-traditional sources of information.

Keywords: amino acids, chirality, structure and properties

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Structure Evolution and Magnetoelectricity in BaO-TiO-FeO-CoO System at R.T

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Crystal structures evolution and their transformation with compositions have been studied on BaO-TiO-FeO-CoO system over a composition zone using Rietveld analysis of x-ray powder diffraction data. The phases as appeared after synthesis showed at RT, a combination of perovskite and spinel phases corresponding to piezoelectric [PE] and piezomagnetic [PM] phases as grown in situ leading to a composite magnetoelectric [ME] material. The ME property of such composites at RT have been measured by dynamic method. A quantitative comprehension of the ME property of the composite in terms of the structures of the component phases have established that ME property being the result of mechanical coupling between the PE and PM phases has considerable contribution from their individual structural property which have been evolved during in-situ preparation.

Keywords: X-ray structural crystallography, magnetoelectric property, composite inorganic phases

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Negative Refraction : an Intrinsic Property of Uniaxial Crystals

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Negative refraction (NR) is a phenomenon where light is refracted to propagate along the same side as the incident light with respect to the normal of the interface, contrary to the normal light refractions. It can be used to realize the "superlens" with a resolution smaller than the wavelength and many other optic applications. Recently, NR has been realized in metamaterials, photonic crystals and traditional crystals. Although the wave vector k does not form a left-handed triplet with the electric field E and magnetic field H for the light in conventional crystals, the light can be bent on the same side with the incident light. We theoretically and experimentally show that negative refraction can be realized at the surface of uniaxial crystals by orientating the crystals with their optic axes at a certain angle θ_0 to the normal of the light incoming surface. The concept of negative refraction can be extended to be an intrinsic property of all uniaxial crystals. That is, NR can be realized in all the uniaxial crystals including with the tetragonal, hexagonal and trigonal symmetries. It is revealed that the angular range for incident light to yield negative refraction attains its maximum that only depends on the difference of two indices of refraction $|n_e - n_o|$ when $\tan^2 \theta_0 = n_o/n_e$. The maximum refracted angle is dependent on the ratio n_e/n_o . The careful experiments on positive uniaxial crystal YVO₄ and negative uniaxial crystal calcite (CaCO₃) give results in good agreement with the calculated ones.

Keywords: crystal structure properties, optical crystallography, refractive index

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Unravelling the Mechanism of the Bathochromic Shift in the Lobster Carapace

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The colouration mechanism in the lobster carapace was revealed at 3.2Å resolution by a protein crystal structure of β -crustacyanin [1]. The crystals are a vivid blue colour and this colour is provided by two bound molecules of the carotenoid astaxanthin. There are three candidate molecular parameters responsible for the bathochromic shift of astaxanthin, which is famously demonstrated via the colour change of lobsters on cooking, turning from blue/black to orange/red: 1. the coplanarisation of the end rings with the polyene chain, increasing the degree of conjugation; 2. an electronic polarisation effect stemming from H bonding of the keto oxygen atoms of the bound astaxanthins, to histidine and water molecules; 3. an exciton interaction due to the close proximity of the two bound astaxanthins.

In order to investigate these colour tuning parameters further, we have determined four new crystal structures of the carotenoids astaxanthin and canthaxanthin all of which are red. These have allowed us to investigate the atomic environment of the end rings and the crystal packing arrangements of the polyene chains. Further experiments are in progress and will also be reported.

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Keywords: lobster, colour, carotenoids

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Crystal Structure of Hematopoietic Prostaglandin D Synthase Complexed of HQL-79

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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 *K_i* 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