

loss/reduction of its haemolytic, phospholipase C and sphingomyelinase activity.

Keywords: bacterial toxins, crystal structures, site-directed mutant

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An Improved Method for Calculating Ligand Solid Angles

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A new approach has been developed to numerically calculate solid angles of the ligands in organometallic complexes. The novelty of the method is in using atomic radii corresponding to the distance where the Morse potential becomes zero, rather than in using the "typical" atomic van der Waals radii corresponding to the minimum of the Morse function. The calculated values include the ligand solid angles, the corresponding cone angles (rather than Tolman cone angles), the ligand special overlaps, ligand overshadowing, and the molecular solid angle. In addition, the calculated solid and cone angles are normalized to a Metal-Ligand distance of 2.28 Å to allow facile comparison of ligand steric demands in complexes of different metals with different compositions of coordination spheres. The new approach has been implemented in the program Solid-G and solid angles parameters with standard deviations have been computed for most common ligands such as cyclopentadienyl and tri-substituted phosphines. The new approach allows to evaluate the conformational flexibility of the ligands.

Keywords: solid angle, organometallic complexes, ligands

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The Perpendicular Magnetic Anisotropy Effect and the Directional Structure Ordering of CrPt₃ the Epitaxial Films

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The epitaxial cubic symmetric CrPt₃ films exhibit a perpendicular magnetic anisotropy (PMA) with large Kerr rotation angles. In order to understand the PMA effect of such a cubic CrPt₃ thin film, the directional chemical order parameters S and polarization dependent x-ray absorption fine spectroscopy (XAFS) were measured in both in-plane and plane-normal directions. The best PMA effect can be found when the plane normal order parameter is largest while the in-plane one is still low. At the same time, Cr-Cr bond-distances have slight distortion by XAFS analysis. This anisotropic directional long range chemical order might be due to the anisotropic interdiffusion and the compound formation between the Cr and Pt layer. For a short-range order analysis, the PMA effect might be attributed to the difference of the Cr-Cr bond-distance between plane-normal and in-plane directions.

Keywords: ordering, magnetic properties, CrPt alloy

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Distribution of Sr Ions in Tungstenbronze-type-like (Ba_{1-x}Sr_x)_{6-3x}R_{8+2x}Ti₁₈O₅₄ (R = Sm, Nd) Solid Solutions

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Tungstenbronze-type-like (Ba_{1-x}Sr_x)_{6-3x}R_{8+2x}Ti₁₈O₅₄ (R = rare earth) solid solution is one of the microwave dielectric materials. The crystal data is as follows: orthorhombic, *Pbnm* (No. 62), *a* ≈ 12, *b* ≈ 22, *c* ≈ 7 Å and *Z* = 2. The crystal structure of the solid solution is composed of two kinds of large cation sites: four pentagonal sites with Ba ions and ten rhombic sites with Ba, Sr and R ions in the framework

formed by TiO₆ octahedron.

These single crystals for R = Sm and Nd system were synthesized by conventional cooling method and FZ method, respectively. The X-ray diffraction data were obtained by a diffractometer with imaging plate (Rigaku; R-AXIS RAPID). Structural parameters were refined by full-matrix least-squares (RADY) [1].

All Sr ions occupied rhombic sites. Especially, one rhombic sites had more amount of Sr ions as compared with another rhombic sites in both of the R = Sm and Nd system. These solid solutions have relationship between distribution of cations and microwave dielectric properties [2]. Therefore, improvement of these properties with increasing composition *x* is lead by substituting Sr ions for Ba ions.

[1] Sasaki S., *XL Report, ESS, State University of New York*, 1982, 1–17. [2] Ohsato H., *J. Eur. Ceram. Soc.*, 2001, **21**, 2703–2711.

Keywords: tungsten bronze, microwave absorption material, structure-properties relationship in solids

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Structural Investigation of Cyclamic Acid and Related Cyclamates

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There exist extensive studies on structure-taste relationship for the artificial sweetening agents, like sucralose (600 times sweeter than sucrose), saccharin (300), acesulfame-K (200) aspartame (180), and cyclamates (30). In order to perceive the sweetness, molecules must activate receptor sites in taste-bud proteins on the tongue. The activation is believed to take place when a molecule of suitable shape has a characteristic functional distribution. According to some theories, there are three essential structural components of a sweeter molecule, oriented in a triangular fashion. More elaborated theories on sweetness are given in an overview [1].

Because the shape of the molecule with the potential sweetness is important and the X-ray structural data for cyclamic acid (cyclohexylsulfamic acid) and cyclamates are not available, the following crystal structures were determined: cyclamic acid, sodium cyclamate, potassium cyclamate, ammonium cyclamate, rubidium cyclamate, caesium cyclamate, tetraethylammonium cyclamate, tetrapropylammonium cyclamate, tetrapentylammonium cyclamate and guanidinium cyclamate.

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[1] Ellis J.W., *J. Chem. Educ.*, 1995, **72**, 671-675.

Keywords: X-ray structure, artificial sweetener, cyclamates

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Structure and Microwave Dielectric Properties on ALa₄Ti₄O₁₅ (A=Ba, Sr and Ca)

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Developments of microwave dielectrics for base station are desirable because of increasing amount of cellular phone. The materials are expected to have high quality factor (*Q*) and high dielectric constant (ϵ_r). We have reported a candidate of homologous compounds Sr-doped BaLa₄Ti₄O₁₅ with high *Q* of 46000GHz, high ϵ_r of 46, and a temperature coefficient of resonant frequency τ_f of -11 ppm/°C. On the other hand the τ_f can be improved to near zero: 1.3 ppm/°C with high ϵ_r of 44 and *Q* of 47000 GHz by substituting Al ions. And when Ba ions are substituted by Sr, it also shows good: *Q* of 46220 GHz, ϵ_r = 43.7, and τ_f = -8.4 ppm/°C. The crystal data of Ba-system are as follows: crystal system: trigonal, space group: *P* $\bar{3}c1$, and lattice constants: *a* = 5.609 Å, *c* = 22.648 Å. This crystal structure belongs to hexagonal layered perovskite-type structure. The packing

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.

[1] Cianci M., Rizkallah P.J., Olczak A., Raftery J., Chayen N.E., Zagalsky P.F., Helliwell J.R., *PNAS USA*, 2002, **99**, 9795-9800.

Keywords: lobster, colour, carotenoids

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

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