

waves devices. Single crystals of various properties have been grown by the Czochralski method from different melt compositions ($\text{La}_3\text{Ga}_4(\text{GaSi})\text{O}_{14}$ and $\text{La}_3\text{Ga}_4(\text{Ga}_{1.14}\text{Si}_{0.86})\text{O}_{14}$) using different conditions: the growth direction ($\langle 0001 \rangle$ -Z-crystals, $\langle 01-11 \rangle$ - $Y54^\circ$ -crystals), the growth atmosphere (Ar - colorless crystals, $99 \pm 98\% \text{Ar} + 1 \pm 2\% \text{O}_2$ -colored crystals), and post-grown treatment (vacuum or air at the 1000° ; ultraviolet or γ -irradiations). The other technology parameters ("Kristall-3M", the pulling and rotation rates - 1.2 mm/h and 1-15 rpm, respectively) did not vary. The aim of this work is to find a relationship between composition, color, microhardness, optical properties, and specific conductivity of LGS.

The peculiarities of the crystal structure and the refined composition of all samples have been determined by the diffraction methods: X-ray (the single crystals - CAD-4 diffractometer, MoK_α ; ground in powder crystals - HZG-4 diffractometer: Ni - filter, CuK_α , 2θ $10-115^\circ$), neutron (the single crystals - TriCS diffractometer: $\lambda=1.18\text{\AA}$; diffractometer located at the channel 5C2, $\lambda=0.830\text{\AA}$).

It is supposed, that color of $\text{La}_3\text{Ga}_4(\text{GaSi})\text{O}_y$ is caused by the oxygen contain: $y \sim 14$ (I-colorless), $y \sim 13.7$ (II-orange), $y \sim 13.6$ (III-yellow), $y \sim 13.4$ (IV-colorless). The colorless crystals can have both the stoichiometric composition (I) and to contain a plenty of oxygen vacancies- $\text{V}_\text{O}^\bullet$ (IV). These results agree with the optical properties (spectrophotometer "Specord-M40"): the bands 28500, 26000, 25000 cm^{-1} are connected with $\text{V}_\text{O}^\bullet$ and the band 20800 cm^{-1} -with color centres. At that the crystals of like visual coloration can have a different shade of color according to the chromaticity diagrams: for example, with the increase a ratio Ga/Si in $\text{La}_3\text{Ga}_4(\text{GaSi})\text{O}_{14}$ orange crystals changes the shade of color from yellow to pale blue over pale green. It has been concluded that the increase in the concentration of oxygen vacancies is of particular value for color crystals, the microhardness, the tangent of dielectric losses and specific conductivity. The frequency and elastic coefficients depend on common crystal composition. The $Y54^\circ$ -crystals, $Y54^\circ$ -cut possess the greater value of microhardness ($MH=14.6$ GPa) and the more structural perfection (the half-width of the Bragg $02\bar{2}2$ peak is $\beta_{\text{exp}}=36.22^\circ$) in comparison with Z-crystals, Z-cut ($MH=14.3$ GPa; $\beta_{\text{exp}}=94.54^\circ$ for 0002 peak). $Y54^\circ$ -crystals, $Y54^\circ$ -cut have the greater value of activation energy ($E_a=1.01$ eV) than Z-crystals, X and Y cuts ($E_a=0.92$ eV). Obtaining of homogeneous on compositions LGS crystals is possible at partial replacement Si on Ge or at contents of Ga excesses in initial composition.

Keywords: piezoelectric; point defect; physical properties

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Magnetic Structure of the Molecular Compound $[\text{Co}_2(\text{bta})]_n$ (H_4bta : Pyromellitic acid). Oscar Fabelo^a, Laura Cañadillas-Delgado^a, Jorge Pasán^a, Fernando S. Delgado^a, Ines Puente-Orench^{b,c}, Javier Campo^{b,c}, Juan Rodriguez-Carvajal^c, Catalina Ruiz-Pérez^a. ^aLaboratorio de Rayos X y Materiales Moleculares,

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The design and construction of new polymeric compounds of tuneable dimensionality, through adapted synthetic routes, is of strong interest in molecular materials [1]. In particular, the hydrothermal synthesis is currently being developed in solid-state and coordination chemistry for the design of new architectures. The magnetic behaviour of $[\text{Co}_2(\text{bta})]_n$ is complex and controversial. DC magnetic measurements without applied magnetic field in the range of temperature 2-300K show different features, a maximum at 16 K which has been explained as a long-range antiferromagnetic order confirmed by a lambda-shaped maximum in the specific-heat plot. At 13 K, another maximum appears together with a maximum in the out-of-phase signal (no frequency dependent). Some authors suggest that this is a field-dependent spin-canting region. [2-4]. Along this line, we have the possibility to shed light on the magnetic properties of a cobalt(II) complex of formula $[\text{Co}_2(\text{bta})]_n$. We have performed a neutron experiment in D1B diffractometer at ILL intending to clarify this situation. We are able to discard the presence of structural phase transitions at low temperatures and to obtain, preliminarily, the antiferromagnetic structure of $[\text{Co}_2(\text{bta})]_n$ below 16K without applied field, but no traces of spin canting has been observed, including that the SC is incompatible with the magnetic space group of the AF phase.

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Keywords: molecular materials; magnetism; neutron diffraction

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Crystal Structures and Magnetic Properties of a Series of Copper(II)-Methylmalonate Complexes with 4,4'-Bipyridine. Jorge Pasán^a, Pau Diaz-Gallifa^a, Mariadel Déniz^a, Laura Cañadillas-Delgado^a, Oscar Fabelo^a, Joaquín Sanchiz^b, Francesc Lloret^c, Miguel Julve^c, Catalina Ruiz-Pérez^a. ^aDepartamento de Física Fundamental II, Facultad de Física, Universidad de La Laguna. La Laguna, Tenerife. Spain. ^bDepartamento de Química Inorgánica, Universidad de La Laguna, Tenerife, Spain. ^cICMol, Departament de Química Inorgánica, Universitat de València, Valencia, Spain. E-mail: jpasang@ull.es

The construction of one-, two-, or three-dimensional (1-D, 2-D, or 3-D) coordination polymers with various architectures is based upon the directionality and control

of metal–ligand interactions. Within our systematic study of the coordination chemistry of the substituted R-malonate ligands, we have observed that the flexibility and versatility of such ligands can produce a great variety of topologies. In this work, we present three copper(II)-methylmalonate coordination complexes synthesized with the same co-ligand. However, $[\text{Cu}(4,4'\text{-bpy})_2(\text{Memal})(\text{H}_2\text{O})]_n \cdot n\text{H}_2\text{O}$ (1) is one-dimensional, whereas $[\text{Cu}_2(4,4'\text{-bpy})(\text{Memal})_2(\text{H}_2\text{O})_2]_n$ (2) and $\{[\text{Cu}(4,4'\text{-bpy})][\text{Cu}(4,4'\text{-bpy})_2(\text{Memal})(\text{NO}_3)(\text{H}_2\text{O})]_n \cdot n\text{NO}_3 \cdot 4n\text{H}_2\text{O}$ (3) are three-dimensional (Memal = methylmalonate dianion and 4,4'-bpy = 4,4'-bipyridine). The role played by the methylmalonate ligand being different in the three complexes: in 1, it is a simple two-fold connector, in 2 it forms a (4,4) with the copper(II) ions and in the case of 3, it pillars a $[\text{Cu}(4,4'\text{-bpy})]_n$ (4,4) network. The flexibility of the Memal ligand is responsible for this versatility. The crystal structure of 3 was solved after realising that it crystallizes in the form of merohedral twins, with a tetragonal cell and $P4_2/n$ space group. However, two areas can be identified within the crystal, they can be carefully separated to yield two crystals of orthorhombic cell and $Pc2_1n$ space group, with inverted structure. Funding for this work was provided by the Spanish Ministerio de Ciencia e Innovación through projects MAT2007-60660, and “Factoría de Cristalización” (Consolider-Ingenio2010, CSD2006-00015). J.P. thanks the CSD2006-00015 for a postdoctoral contract.

Keywords: metal-organic frameworks; copper; twin resolution

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Crystal Engineering of Metal Barbiturates as Potential NLO Materials. Marlena Gryl^a, Katarzyna M. Stadnicka^a. ^a*Faculty of Chemistry, Jagiellonian University, Krakow, Poland.*
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Polar organic-inorganic crystal phases are known to be highly efficient non-linear optical materials [1]. Combination of inorganic and organic components provides mechanical and optical resistance, guarantees structural flexibility and high nonlinear efficiency. Barbituric acid and barbiturate molecules, possessing suitable hydrogen bond donors and acceptors, seem to be valuable components in crystal engineering of materials with specific, programmed properties. Moreover there are already known barbituric acid derivatives which exhibit NLO properties [2, 3] as well as there is a possibility to design polar cocrystals comprised of barbituric acid and urea molecules [4]. Recently we have discovered the usage of barbituric acid and selected inorganic metal salts to form polar cocrystals. Among several crystal structures of metal barbiturates obtained, the cadmium barbiturate dihydrate (Iba2) and copper barbiturate trihydrate (Fdd2) - previously reported in the literature [5], are polar whereas the rubidium barbiturate monohydrate is centrosymmetric ($P2_1/c$). The obtained phases have been structurally characterised and compared. The recognised coordination polyhedrons form layers linked by barbiturate ions, with additional interactions *via* hydrogen bonds. The polar crystal structures can be considered as potential NLO

materials.

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Keywords: crystal engineering; cocrystals; nonlinear optics

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Synthesis and Crystal Structures of Four Heptanuclear Mixed-valence $[\text{Fe}(\text{CN})_6\{\text{FeL}\}_6]\text{Cl}_2$ Complexes. Jan Moncol^a, Ivan Šalitróš^a, Roman Boča^a. ^a*Department of Inorganic Chemistry, Slovak Technical University, SK-81237 Bratislava, Slovakia.*

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Prussian blue analogues with Schiff bases ligand types are known to form a wide range of coordination compounds with transition metals [1,2], but only one structure of the heptanuclear mixed-valence iron complex formed of the $\{\text{Fe}(\text{CN})_6\}$ core and six N-coordinated mononuclear precursors has been reported [3]. The crystal structures of four heptanuclear mixed-valence $[\text{Fe}(\text{CN})_6\{\text{FeL}\}_6]$ complexes were studied. Various triamines Schiff-condensed with o-salicylaldehyde yielded pentadentate ligands L that form Fe(III) complexes $[\text{Fe}^{\text{III}}(\text{L})\text{Cl}]$. These precursors were used in assembling mixed-valence heptanuclear $[\{\text{Fe}^{\text{II}}(\text{CN})_6\}\{\text{Fe}^{\text{III}}(\text{L})\}_6]\text{Cl}_2 \cdot x\text{H}_2\text{O}$ complexes bridged through the CN group.

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Keywords: crystal structure; mixed-valence; iron complex

FA4-MS02-P17

Novel Co(II) and Ni(II)-Nitrito Complexes with NNN Type Ligand. Cigdem Hopa^a, Mahir Alkan^a, Raif Kurtaran^a, Hulya Kara^b, Robert Hughes^c, Mairi F. Haddow^c. ^a*Department of Chemistry, Balıkesir University, Balıkesir, Turkey.* ^b*Department of Physics, Balıkesir University, Balıkesir, Turkey.* ^c*Department of Chemistry, Bristol University, Bristol, UK.*
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Two novel monomeric $[\text{Co}(\text{bdmpp})(\text{ONO})_2]$ (1), $[\text{Ni}(\text{bdmpp})(\text{ONO})_2]$ (2), (bdmpp=2,6-bis(3,5-dimethylpyrazol)pyridine) complexes have been synthesized and characterized by single crystal X-ray diffraction analysis, elemental analysis, IR spectroscopy, UV-Vis spectroscopy and thermal analysis. Compound 1