

mode analysis of any ferroic structure. As input only the ferroic distorted structure and the (real or virtual) non-distorted one of higher symmetry is required. With this information the program AMPLIMODES identifies the displacive distortion present in the structure and decomposes it in terms of modes of different symmetries associated with irreducible representations of the high-symmetry space group. The decomposition of the structure in collective symmetry-adapted distortion modes is given in terms of global amplitudes and normalized polarization vectors for each of the modes present. The importance and character of each of the allowed symmetry modes can be extracted from a comparison of their amplitudes and the internal structure of their polarization vectors. The polarization vector of each frozen mode is presented in a crystallographic way, as a list of relative atomic displacements within an asymmetric unit. This allows a straightforward construction of virtual structures corresponding to the sole presence with arbitrary amplitudes of any of the relevant modes. This type of analysis allows to distinguish and isolate the correlated atomic displacements that correspond to the structural instabilities at the origin of the ferroic distortion, i.e. the so-called primary modes. In this way, secondary weaker induced distortions of marginal relevance are separated. The Bilbao Crystallographic Server, where this tool can be used on-line, is a free web site with many other crystallographic databases and programs [1,2].

[1] M. I. Aroyo et al., *Acta Cryst.* (2006). A62, 115-128

[2] M. I. Aroyo et al., *Z. Krist.* (2006), 221, 1, 15-27.

Keywords: ferroic materials, structural phase transitions, symmetry modes

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### New organic conductors based on cobaltacarborane anion and its derivatives

Oleg Dyachenko<sup>1,2</sup>, Olga Kazheva<sup>2</sup>

<sup>1</sup>Russian Foundation for Basic Research, Leninskii prosp., 32a, Moscow, Moscow, 119991, Russia, <sup>2</sup>Institute of Problems of Chemical Physics of RAS, Semenov av., 1, Chernogolovka, 142432, Russia, E-mail : doa@icp.ac.ru

Just a few conducting radical cation salts containing metallacarborane anions have been described so far [1,2]. No radical cation salt derived from the cobalt bis(dicarbollide) anion  $[3,3^{\prime}\text{-Co}(1,2\text{-C}_2\text{B}_9\text{H}_{11})_2]^-$  or its halogen derivatives was reported. First molecular conductors with cobalt bis(dicarbollide) anion and its iodine and bromine derivatives were electrochemically synthesized and investigated by X-ray study [3-5]: (TMTSF)<sub>2</sub>[3,3<sup>′</sup>-Co(1,2-C<sub>2</sub>B<sub>9</sub>H<sub>11</sub>)<sub>2</sub>] (1), (TTF)[3,3<sup>′</sup>-Co(1,2-C<sub>2</sub>B<sub>9</sub>H<sub>11</sub>)<sub>2</sub>] (2), (ET)[3,3<sup>′</sup>-Co(1,2-C<sub>2</sub>B<sub>9</sub>H<sub>11</sub>)<sub>2</sub>] (3), (ET)<sub>2</sub>[3,3<sup>′</sup>-Co(1,2-C<sub>2</sub>B<sub>9</sub>H<sub>11</sub>)<sub>2</sub>] (4), (ET)<sub>2</sub>[8-I-3,3<sup>′</sup>-Co(1,2-C<sub>2</sub>B<sub>9</sub>H<sub>10</sub>)(1<sup>′</sup>,2<sup>′</sup>-C<sub>2</sub>B<sub>9</sub>H<sub>11</sub>)] (5), (BMDT)[3,3<sup>′</sup>-Co(1,2-C<sub>2</sub>B<sub>9</sub>H<sub>11</sub>)<sub>2</sub>] (6), (ET)<sub>2</sub>[3,3<sup>′</sup>-Co(8-Br-1,2-C<sub>2</sub>B<sub>9</sub>H<sub>10</sub>)<sub>2</sub>] (7), (BMDT)<sub>4</sub>[3,3<sup>′</sup>-Co(8-Br-1,2-C<sub>2</sub>B<sub>9</sub>H<sub>10</sub>)<sub>2</sub>] (8), and ET[3,3<sup>′</sup>-Co(8-BrC<sub>2</sub>B<sub>9</sub>H<sub>10</sub>)<sub>2</sub>] (9). Salt (1) is a semiconductor with activation energy  $E_a=0.03$  eV, conductivity  $S(293) = 15 \text{ Ohm}^{-1}\text{cm}^{-1}$ , that is the maximum value of conductivity for all metallacarborane radical cation salts studied before [1,2].

References:

[1] J.M.Forward, et al., *J.Organomet. Chem.*, 1994, 467, 207

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[3] O.N.Kazheva, et al., *J.Organomet.Chem.*, 2006, 691, 4225

[4] O.N.Kazheva, et al., *J.Organomet.Chem.*, 2007, 692, 5033

[5] O.N.Kazheva, et al., *JSSS*, 2008, in press

Keywords: organic conductors, carboranes, X-ray crystal structure analysis

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### Phase and glass forming diagrams in the gallium borate and ternary barium gallium borate systems

Rafael M Hovhannisyanyan<sup>1</sup>, Bella V Grigoryan<sup>1</sup>, Hovakim A Alexanyan<sup>1</sup>, Berta V Petrosyan<sup>1</sup>, Vahan P Toroyan<sup>2</sup>

<sup>1</sup>Scientific-Production Enterprise of Material Science, Research & Development, 17 Charents Str., Yerevan, Yerevan, 25, Armenia, <sup>2</sup>Institute of General and Inorganic Chemistry of NAS RA, Argutyanyan st., district 2, 10, Yerevan, 0051, Armenia, E-mail: hovhannisyanyan@netsys.am

The revealing of new stoichiometric compositions still actual problem for new acentric or non-centrosymmetric solids (single crystals, ceramics) development. The glass ceramic (GC) technology combines flexibility, simplicity and cheapness of glass technology with possibility to form crystal structures of the reference sizes and compositions through controlled and oriented crystallization. Alkaline earth binary borates and alkaline-earth ternary borates are the good candidate for this purpose, because they combine nonlinear characteristics with good glass forming ability. This was a motivation for study and construction both phase and glass forming diagrams in the binary gallium borate and ternary barium gallium borate systems. The glasses were melted from chemically pure grade chemicals in platinum crucibles in air at 1300-1600 °C in electrical furnace.

Keywords: barium gallium borates, phase diagram, glass forming diagram

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### SAXS investigation of SBA-15 vacuum calcination process

Francisco Mariano Neto<sup>1</sup>, Marcia C. A. Fantini<sup>1</sup>, Luis C. Cides Silva<sup>2</sup>, Jivaldo R. Matos<sup>2</sup>

<sup>1</sup>Institute of Physics / University of Sao Paulo, Applied Physics Department, Trav. R da Rua do Matao, 187, Ed. Basilio Jafet, Sl. 124-B, Sao Paulo, Sao Paulo, 05508-900, Brazil, <sup>2</sup>Institute of Chemistry / University of Sao Paulo, E-mail: fmneto@if.usp.br

Ordered mesoporous silica (OMS) is a new alternative material for many technologies, ranging from microelectronics to medical applications. In this work, in situ analysis of the calcination process of SBA-15 was carried out in vacuum at the SAXS2 beamline of LNLS, Brazil. The as-synthesized powder was submitted to a heat treatment procedure at a pressure of about  $1 \cdot 10^{-3}$  torr, from room temperature up to 540 °C, at a constant temperature increase of around  $2^\circ\text{C} \cdot \text{min}^{-1}$ . The sample was kept at this temperature for 6 hours. At around 300 °C the polymer starts to decompose and the lattice parameter decreases from  $a=12.8\text{nm}$  to  $a=12.4\text{nm}$ , until the temperature reaches 540 °C, when the polymer decomposes. The lattice parameter reaches a final value of 12.3nm, remaining at this constant figure until the final cooling process. The peak areas do not change up to 300 °C. A strong and subtle increase of peak areas is observed at this temperature. During the isothermal calcination process, part of the ordered structure is destroyed, as indicated by the decrease of the diffracted intensities. A sample previously calcined in nitrogen and air showed a larger shrinkage effect, resulting in  $a=11.8\text{nm}$ . Also, the SAXS curve of this sample presented a larger background when compared to that registered in the measurements of the vacuum heat treated sample. This result is attributed to the presence of disordered pores, with maximum gyration radius of 7nm, to micropores and/or to inter-grain scattering. Ex-situ SAXS analysis of a similar sample submitted to vacuum heat treatments at 300 °C, 400 °C and 540 °C was also carried

out in order to check the conditions for total polymer removal. Thermo-gravimetric analysis and nitrogen adsorption isotherms completed the study.

Keywords: small-angle diffraction, *in-situ* experiments, temperature

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#### Crystal structures and mesomorphism of metal-salen complexes with 4-substituted long alkoxy chains

Yuriko Abe<sup>1</sup>, Tomoaki Tanase<sup>1</sup>, Kazuchika Ohta<sup>2</sup>

<sup>1</sup>Nara Women's University, Department of Chemistry, Kitaouya-Nishimachi, Nara, Nara, 630-8506, Japan, <sup>2</sup>Smart Material Science and Technology, Interdisciplinary Graduate School of Science and Technology, Shinshu University, Ueda, 386-8567, Japan, E-mail : yabe@cc.nara-wu.ac.jp

Liquid crystals with transition-metal core groups, called as metallomesogens, have attracted increasing attention because of the possibility of combining their physico-chemical properties of the metal with those of organic framework. Since the metallomesogens are achieved through changes of molecular conformation, shape, and structure, their physico-chemical properties can be turned by the choice of metal ions, substituents, and position of substituents on core moieties. Schiff base ligands provide a wide range of ways to modify liquid crystal compounds. However, to date there has been no systematic investigation concerning molecular assemblies and metallomesogens of metal-salen (salen=*N,N'*-ethylenebis(salicylideneiminato)) complexes substituted by two long alkoxy chains at the 4-positions though the metal-salen complexes with 5-substituted alkoxy or alkyl chains usually show smectic A (S<sub>A</sub>) mesophases at higher temperature. Recently, we prepared three series of the VO(IV), Ni(II), and Cu(II) salen complexes with two long alkoxy chains introduced at the 4-positions, [M((4-C<sub>n</sub>H<sub>2n+1</sub>O)<sub>2</sub>salen)] (M=VO(IV), Ni(II), Cu(II), *n*=3-20) and found an unprecedented bilayer mesophase having symmetry Pa2<sub>1</sub> in the layers for the VO(IV) salen complexes with *n*=16-20.<sup>1</sup> On the other hand, the Ni(II) and Cu(II) salen complexes with longer alkoxy chains showed an unusual metallomesogen of a lamello-columnar (Col<sub>l</sub>) mesophase.<sup>2,3</sup> There have been few reports on the metallomesogen of the Col<sub>l</sub> mesophase. These liquid crystalline phase structures have been affiliated with the molecular assemblies in the crystalline states.

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Keywords: metal-salen complexes, 4-substituted long alkoxy chains, metallomesogen

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#### Profile analysis of chemically prepared emeraldine-salt and emeraldine-base forms of polyaniline

Yvonne P. Mascarenhas, Edgar A. Sanches, Juliana C. Soares USP, E-mail : yvonne@ifsc.usp.br

ES-PANI form powder was prepared by chemical oxydation using aniline previously distilled added to HCl aqueous solution. amonium peroxydisulphate was dissolved in HCl aqueous solution and then added to the above solution slowly at room temperature.

ES-PANI was obtained and kept in NH<sub>4</sub>OH yielding EB-PANI. XRD patterns were obtained with a Rigaku RotaFlex, CuK $\alpha$ , 50 kV, 100 mA, graphite monochromator. Data collected from 2 $\theta$  = 5 - 60°, step 0.02° and 5 sec. Profile Matching fit was performed using FULLPROF. Initial cell parameters from Evain *et al.*, 2002. Anisotropic size broadening was modeled. Refined structural parameter and agreement factors for ES-PANI are *a*=5.61214; *b*=17.78087; *c*=23.04183;  $\alpha$ =83.25719;  $\beta$ =84.71980;  $\gamma$ =88.08441; *V*=2273.126Å<sup>3</sup>; *R*<sub>p</sub>=1.08; *R*<sub>w</sub>*p*=1.38;  $\chi^2$ =1.40 and for EB-PANI are *a*=5.71920; *b*=17.77932; *c*=23.52416Å;  $\alpha$ =84.13010;  $\beta$ =85.22524;  $\gamma$ =87.30433; *V*=2369.428Å<sup>3</sup>; *R*<sub>p</sub>=1.77; *R*<sub>w</sub>*p*=1.39;  $\chi^2$ =1.14. Obtained values are in agreement with literature, except cell parameter *b*, which was almost doubled. EB-PANI form average crystallite size (25.42Å) obtained from the refinement confirmed its lowest percentage of crystallinity compared with doped ES-PANI form (36.45Å).

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#### Coordination polymers towards applications: Chirality by design

Anthony R Esterman, Manuel A Fernandes

University of the Witwatersrand, School of chemistry, 1 Jan Smuts Ave., Braamfontein, Johannesburg, Gauteng, 2050, South Africa, E-mail : anthony.esterman@students.wits.ac.za

Crystal engineering involves the design and subsequent synthesis of crystals with the specific aim of developing new crystalline materials. The main focus of this field lies in the ability to predictably synthesize supramolecular structures from smaller, well designed building blocks.[1] The formation of self-assembled coordination polymers has attracted much interest in recent years. Here crystal engineering takes a vital role in the construction of porous frameworks that may show functionality in various applications. There are two main components to any coordination polymer, namely the connectors (metal ions) and the linkers (organic ligands). Because there are a number of tunable parameters (for example: metal centre coordination environments, ligand size and flexibility, ligand functional group type and position, ligand charge, choice of counter ions and solvents) it is possible to generate a diverse number of framework architectures.[2] In this study we have selected dipyriddy type linkers and a number of divalent transition metals [Cd(II), Cu(II), Co(II) and Ni(II)] as building blocks. The organic linkers have been carefully chosen to coordinate with the metals to form chiral crystals. This is most effectively done by selecting chiral moieties, removing the possibility of creating centrosymmetry in the crystal structure. We have also used flexible achiral moieties to create chiral crystals. This is significant, as only about 17% of structures in the CSD (Nov 2007) are chiral, with only a small fraction of these arising from achiral molecules. Selected results will be presented.

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[2] S. Kitagawa, R. Kitaura, S. Noro, *Angew. Chem. Int. Ed.*, 2004, 43, 2334. and citations therein.

Keywords: coordination polymers, crystal engineering, chirality