

P08.14.152*Acta Cryst.* (2008). A64, C465**Solid-state thermochromism of polydiacetylenes containing robust 2D hydrogen bond network**

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We have reported that topochemical polymerization principles and the design of the monomer stacking using supramolecular synthons for the polymerization of 1,3-diene monomers. The most sophisticated molecules included the naphthylmethylammonium group as the counteraction of diene carboxylates. This group is appropriate for the rational design and the control of the arrangement of monomer molecules in the crystals. Here we report the polymerization behavior of diacetylenes containing a naphthylmethylammonium carboxylate group in the side chain, which makes robust 2D hydrogen bond networks. The resulting polydiacetylenes (PDAs) showed the thermochromism depending on the structure of the alkyl substituents and spacers in the side chain. In order to discuss the effect of the side chain conjugating group on the chromatic property of PDA, we further investigated the solid-state structure and chromatic properties of PDAs containing aromatic groups that are directly connected to the conjugating main chain. We have concluded that the thermochromic transition can be classed into several kinds of different phases on the basis of the conformation of conjugating main chains and the alkyl and aromatic side groups in the solid state.

Keywords: conjugated organic compounds, polymer structures conformation, hydrogen bonds in organic crystals

P08.14.153*Acta Cryst.* (2008). A64, C465**Relation between X-ray emission mechanism and crystal structure in LiTaO₃**Yoshiaki Ito¹, Hirohisa Mizota¹, Yoshikazu Nakanishi², Katsumi Handa¹, Tatsunori Tochio³, Shinji Fukao², Shinzo Yoshikado², Takanori Tanaka⁴

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LiTaO₃ is well known as a ferroelectric material and is used in polarization converters etc.. At temperatures below the Curie temperature T_c (T_c~930 K) of LiTaO₃, the centres of positive and negative charges in a LiTaO₃ crystal are separated spatially and the crystal is polarized. Brownridge et al. have reported x-ray emission during temperature changes of pyroelectric crystals like LiNbO₃ or LiTaO₃ under vacuum. Subsequently, their group and ours have independently investigated x-ray generation by ferroelectric crystals. Changing the temperature changes the absolute magnitude of polarization. Electrons in the crystal can be accelerated by an electric field due to the surface charges of the crystal formed upon temperature changes, in which the large intensity of the photon flux of x-rays was obtained at 10⁻³ Pa. X-rays are radiated as a result of the bremsstrahlung caused by the collision of charged particles with a target metal. The x-ray radiation rate becomes maximum at a gas pressure of approximately 5 Pa. As there have been no reports on structural analysis in the high temperature range in which x-ray

emission can be observed on the surface of the crystal, Nakanishi et al. carried out high temperature single crystal structure analysis of LiNbO₃ and suggested that the valence electron in Nb changes in the compound and x-ray emission have a close relation to the electric charge of Nb in LiNbO₃. Therefore, we executed the single crystal structure analysis of LiTaO₃ in the temperature range between room temperature to about 440 K which x-ray emission can be observed, far below the phase transition, T_c in order to elucidate the mechanism of the x-ray emission in the pyroelectric crystals.

Keywords: ferroelectric material, LiTaO₃, X-ray emission

P08.14.154*Acta Cryst.* (2008). A64, C465**Reversible structural changes by electrostatic fields in strontium titanate at room temperature**Hartmut Stoecker, Alexandr A Levin, Emanuel Gutmann, Torsten Weissbach, Tilmann Leisegang, Stephan Ritter, Chris Elschner, Manfred Bobeth, Wolfgang Pompe, Dirk C Meyer
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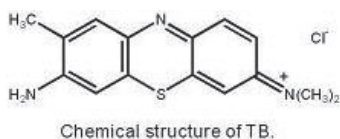
Beyond the use as substrate material, strontium titanate (SrTiO₃) is an interesting material for electronic and other applications because of its high dielectric permittivity. Its properties strongly depend on the defects in its perovskite-type of structure, even at room temperature. Mobile oxygen can cause the formation of non-stoichiometric regions when an electric field of sufficient strength (1000 V/mm) is applied. Our investigations revealed reversible structural changes at room temperature caused by a systematic field-induced redistribution of oxygen. The structural changes are highlighted by means of wide-angle X-ray scattering, X-ray absorption spectroscopy and time-resolved measurements of the electric current. We found a reversible conversion of the perovskite-type of structure to a long-range ordered variant with changed lattice parameter. The time dependence of the current is compared to the temporal change of the structure of SrTiO₃ at near-surface regions (depth in the order of 10 micron). A model describing the stages of a supposed solid-state electrolysis is presented. Local changes of the refraction index caused by stress birefringence were discovered by optical polarization microscopy. These local stress fields may be attributed to dislocation cores acting as paths for the oxygen transport to the anode. From spectroscopic measurements showing a change of titanium valence in near-surface regions, we can prove the oxygen diffusion model. Our results open a way to structurally modify the technologically relevant perovskite oxides using electrostatic fields. The tunable lattice spacings observed might be used in the field of adaptive X-ray optics. Also, substrates with tunable dielectric properties at constant basal lattice parameters could be realized.

Keywords: perovskites, electrical characterization, *in-situ* experiments

P08.14.155*Acta Cryst.* (2008). A64, C465-466**The crystal structure of a metachromatic dye toluidine blue**Saori Sato¹, Xianglang Li¹, Shinya Matsumoto¹, Talivaldis Freivalds², Jekaterina Erenpreisa², Motoo Shiro³¹Yokohama National University, Graduate School of Environment and

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Toluidine blue O (TB), one of popular cationic dyes, has been used in biological and medical fields as a important cytological probe because of its metachromatic effects. Its metachromasy has been considered to be caused by the formation of a certain dye aggregate. It is very important to understand the relationship between the metachromatic spectral change and the aggregates, in order to obtain structural information of biomolecules from metachromatic staining. But regarding TB, structural data of both TB itself and TB - biomolecule complexes have not been reported. We then approached the structure analysis of TB. TB was crystallized as blue needles by means of solvent diffusion method using ion-exchanged water and acetone as good and poor solvents, respectively. However, the thickness of the needles was unsuitable for X-ray structure analysis. On the other hand, thick crystals were obtained after exchanging the chloride ion to hexafluorophosphate ion. Its crystal analysis is now under investigation.



Keywords: crystal structure of organic compounds, dye compounds, molecular biology

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Keywords: organic conductors, X-ray analysis, materials properties

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Optical activity of *N*-benzoylglycine crystals

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Every chiral organic crystal has inherent optical activity. The sign and the magnitude of the optical activity of an organic crystal should reflect the molecular structure and the packing arrangement because the freedom of molecules is severely restricted in the crystal lattice. We report here the optical rotatory power of chiral crystals self-assembled from achiral *N*-benzoylglycine determined by HAUP (high accuracy universal polarimeter) method. The magnitude of rotatory powers was 10 to 100 times larger than that for ordinary organic crystals. It revealed that the helically arranged aromatic p electrons as well as the helical ionic and hydrogen bond networks in the crystal contributed to the enhancement of the magnitude of these rotations.

Keywords: optical activity, *N*-benzoylglycine, chiral crystal

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Structure of new organic semiconductors with cobalt bis(dicarbollide) bromine anion

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New molecular semiconductors on the base of 8,8'-dibromo cobalt bis(dicarbollide) anion, (BEDT-TTF)₂[8,8'-Br₂-3,3'-Co(1,2-C₂B₉H₁₀)₂] (1), (BEDT-TTF)[8,8'-Br₂-3,3'-Co(1,2-C₂B₉H₁₀)₂] (2) and (BMDT-TTF)₄[8,8'-Br₂-3,3'-Co(1,2-C₂B₉H₁₀)₂] (3) were synthesized and investigated. Recently we have started investigation of the structure-property relationship in a series of fulvalene salts of cobalt bis(dicarbollide) anion and its derivatives [1,2]. These counter anions are particularly interesting owing to their enormous variability. The cobalt bis(dicarbollide) anion [3,3'-Co(1,2-C₂B₉H₁₀)₂]⁻ offers several distinct ways of chemical modification: (1) substitution at carbon atoms; (2) substitution at boron atoms in upper belt of the dicarbollide ligand; and (3) substitution at boron atoms in lower belt of the dicarbollide ligand. As a result, molecules with a wide variety of properties in almost unlimited variations can be prepared. In this contribution, we present synthesis and structure of the first electroconducting salts of the dibromo derivative of cobalt bis(dicarbollide) anion [8,8'-Br₂-3,3'-Co(1,2-C₂B₉H₁₀)₂]⁻. Crystal structure of (BEDT-TTF)₂[8,8'-Br₂-3,3'-Co(1,2-C₂B₉H₁₀)₂] (1) is formed by the BEDT-TTF radical cations in general positions of the unit cell, and the [8,8'-Br₂-3,3'-Co(1,2-C₂B₉H₁₀)₂]⁻ anions in special centrosymmetric positions (Fig.1). Fig. 1. Atomic designations in (BEDT-TTF)₂[8,8'-Br₂-3,3'-Co(1,2-C₂B₉H₁₀)₂] (1)

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New photoluminescent microporous metal phosphate as a hybrid intrinsic yellow phosphor

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Photoluminescence is a new property of microporous materials. Recently some extra-large channel zinc and gallium phosphates are found to emit blue light[1-5] or even synchronize dual wavelengths to give out white light under the excitation of UV light [6]. Th intriguing optical property has allowed us to discover microporous metal phosphates a new class of inorganic phosphors with distinct emission centers different from conventional understanding. In current lighting technology, yellow light phosphor integrated with blue LED to produce white light is of the most importance. Demands on inorganic yellow-light phosphors are increasing. Yet they are limited in number and kind. Existing inorganic yellow phosphors are all extrinsic illuminants, i.e. a condensed host lattice with doped lighting elements. No inorganic host without doped metal activators could emit yellow light. The extraordinary intrinsic yellow emission of NTHU-4 is speculated to closely correlate with defects resulting from the disorderliness near large pores. In this presentation, we report the synthesis, structure and some property of a new yellow phosphor, NTHU-6 [7], which has a unique MOF-like organic-inorganic hybrid open framework with high PL quantum efficiency (PLQE). It is the first hybrid microporous yellow light phosphor ever discovered.

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