

molecular packing structure of the guest amines was dependent on the structure of the guest amines. Next, we investigated the intercalation behavior of azobenzene derivatives, which were designed based on the intercalation characteristic of several guest amines previously reported. In the present study, azobenzene derivatives containing amino and diamino groups were synthesized and used as the guest for the intercalation. The intercalation of azobenzene derivatives into the interlayer space of poly(muconic acid) crystals was successfully carried out by the dispersion method. We investigated the intercalation and photoisomerization behaviors depending on the structure of the used azobenzene derivatives.

Keywords: intercalation materials, organic crystals, photochemistry

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Fabrication of thin-film organic crystals by vapor deposition and their solid-state polymerization

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The solid-state polymerization of unsaturated monomers is one of the useful methods for the synthesis of polymers with a highly controlled structure. In particular, topochemical polymerization has unique features, such as complete tacticity control and the in-situ fabrication of polymer crystals. We previously reported the topochemical polymerization of some derivatives of muconic and sorbic acids as the 1,3-diene monomers in the solid state under photoirradiation, which produced stereoregular polymers in the form of polymer crystals. The polymerization reactivity and the structure of the resulting polymers are strictly determined by the monomer crystal structure, that is, the fashion of the molecular arrangement in the monomer crystals. However, the polymorphism often prevents us designing the organic solid materials and controlling their physical properties. In the present study, we have fabricated the organic thin films of bis(3,4-methylenedioxybenzyl) (E,E)-muconate by the vapor deposition method in order to control crystal growth and crystal structures using interaction between the surface of a substrate and the monomer molecules. We have investigated the structure of the obtained thin films of the monomer crystals by AFM observation, IR spectroscopy, and powder X-ray diffraction measurements. The polymerization was carried out in the solid state under UV or gamma-ray radiation. The epitaxial crystal growth on various substrates, the polymerization reactivity of the obtained thin films, and the control of polymer structures are discussed.

Keywords: topochemistry, epitaxial growth, polymer synthesis

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Photocyclization of isopropylbenzophenone derivatives in crystals and the shape changes

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Crystalline state photocyclizations and the morphological changes of isopropylbenzophenone derivatives were investigated. We found diastereospecific photocyclization via single-crystal-to-single-crystal transformation. Absolute asymmetric photocyclization was also achieved. The surface morphological changes of the crystals were traced by atomic force microscopy on photoirradiation.

Keywords: photocyclization, isopropylbenzophenone derivatives, morphology change

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Solvent inclusion induces helical molecular assembly in crystals of halobenzoates of *myo*-inositol

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Reactions in crystals often proceed with high facility, regio- and stereo-selectivity due to topochemical control as compared to those in solution. Earlier, we reported clean solid-state benzoyl transfer reactions in crystals of racemic 2,6-di-O-benzoyl *myo*-inositol 1,3,5-orthoesters [1]. Structure correlation studies [2] suggest that pre-organization of the electrophile (E1) and nucleophile (Nu) close to tetrahedral angle 110 °C at a distance of about 3 Å is essential for reaction to occur. Structures of reactive orthoesters revealed helical self-assembly of the molecules via O-H...O hydrogen bonds bringing electrophile (-C=O) and nucleophile (-OH) in favourable proximity with weak interactions supporting the migrating group. To investigate molecular organization and solid-state reactivity further, racemic 2,6-di-O-(4-halobenzoyl)-*myo*-inositol 1,3,5-orthoformate (halo = fluoro, chloro, bromo) were synthesized. Solvent free crystals obtained from methanol and ethyl acetate [3] did not possess the right organization for acyl transfer; however, inclusion crystals from almost all common organic solvents revealed a helical self-assembly of host molecules linked via O-H...O hydrogen bonding with E1...Nu geometry close to that observed for reactive orthoesters [1]. One of the inclusion crystals with favorable geometry exhibited neat acyl transfer reaction.

[1] C. Murali, M. S. Shashidhar, R. G. Gonnade, M. M. Bhadbhade, *Eur.J.Org Chem.* **2007**, 7, 1153 and references cited therein. [2] H. B. Bürgi, J. D. Dunitz, In *Structure Correlation*, VCH:Weinheim, **1994**, 2,767. [3] R. G. Gonnade, M. S. Shashidhar, M. M. Bhadbhade, *CrystEngComm* **2008**, 10, 288.

Keywords: solid-state reactions, inositols, inclusion crystals

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Oxide and metal silicide precipitation on structural defects in mc silicon studied by TEM

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Solar cell production from multicrystalline (mc) silicon presently experiences a yearly growth of about 40%. A lack of cheap scrap silicon from the electronic industry has arisen the last years. Metallurgical silicon is very expensive to purify, and, in order to produce cost effective solar cells, the new trend is to use dirtier source materials in mc ingot production. Higher levels of impurities and structural defects in such materials act as recombination centres and reduce the efficiency of mc silicon solar cells. To come up with good solutions for improving the silicon wafer production, it is important to understand how structural defects are formed and where precipitates of other phases are nucleated and grow during solidification and cooling. In the present work impurity precipitation on extended defects in as-cast mc silicon grown from metallurgical feedstock using a direct route process (i.e. no filtration and one step directional solidification) has been studied using transmission electron microscopy combined with dislocation density measurements and chemical analysis. All observed dislocations and grain boundaries, except for some coherent twins, were contaminated with silicon oxide precipitates. Different types of multi-metal precipitates containing nickel, copper and iron were present randomly distributed in grain boundaries. No measurable gettering of metals by oxides was observed. Slower diffusing elements were not present in the precipitates, in spite of being present at relatively high levels in the bulk. Observations are discussed in terms of the potential for defect engineering to reduce cost by allowing the use of lower purity feedstock.

Keywords: silicon crystal growth and its effect on device pe, transmission electron microscopy, solar cell fabrication

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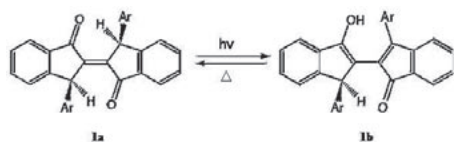
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Crystalline-state photochromic reaction of *trans*-biindenilidenedione derivatives

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It has been found that *trans*-biindenylidenedione (TBID) derivatives show photochromism and the color changes from yellow to red upon irradiation with UV and visible light in the solid state. In our previous study, crystal structure determination of red form was performed in order to reveal the photochromic reaction mechanism. The crystal structure after irradiated with UV light was analyzed to show both the reactant (**1a**) and the photoproduct (**1b**) which were located as a disordered structure, indicating that the photochromism is caused by an intramolecular (Norrish Type II) hydrogen transfer reaction. In this study, several TBID pseudo-polymorphs were prepared and the crystal structures were determined before and after the irradiation in order to make clear the relationship between the structures and photochromic properties. From the comparison of the crystal structures and the life-time of red-colored photoproduct, it is elucidated that the following three factors are important for the photochromism; (1) molecular conformation of the initial crystal, (2) cavity size around the reactive part of the molecule, and (3) cooperative movement of the solvent molecules in the crystal.



Keywords: crystalline-state reaction, photochromism, biindenilidenedione Derivatives

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Structural and physical properties of single crystal $K_xNa_{1-x}NbO_3$ around the $x=0.3$ phase boundary

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Lead zirconium titanate (PZT) is commonly regarded as the leading piezoelectric material for a wide range of applications, and one which all others are assessed against. However, there are growing concerns over the toxicity and environmental issues of lead-based substances [1], which is why attention has turned to other lead-free piezoelectric materials. Sodium potassium niobate (KNN) is of particular interest not only because its piezoelectric properties are comparable to that of PZT [2], but also because the phase diagram contains three morphotropic phase boundaries (MPB), at $x=0.2$, $x=0.3$ and $x=0.5$. MPBs are a very interesting area of study, since dielectric and piezoelectric properties are enhanced in these regions, and the atomic-level structural mechanisms underlying these transitions are poorly understood. Until now, only the MPB at $x=0.5$ in KNN has been studied in any detail, and no information was available on the other two. Several single crystal samples have been grown via the flux method around the $x=0.3$ MPB. X-ray structural analysis has been performed to supplement earlier X-ray and neutron work on powder samples. Birefringence, dielectric, NMR and polarisation measurements have also been taken with a variety of techniques, in order to explain the enhanced physical properties of this potentially interesting material at this previously unstudied MPB.

[1] M. Demartin Maeder, D Damjanovic, N. Setter, *Journal of Electroceramics* 2004, 13, 385 – 392.

[2] Saito et al., *Nature* 2004, 432, 84

Keywords: phase transitions, quantitative X-ray analysis, ferroelectric piezoelectric crystals

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Phase transitions in one-layered Aurivillius phases, $Bi_2W_{1-x}Mo_xO_6$ ($0 < x < 1$)

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One-layered ferroelectric-superionic Aurivillius phases Bi_2WO_6 (BW) and Bi_2MoO_6 (BM) are under investigation more than 50 years but there is no agreement concerning their polymorphism. There are well-established in both compounds two phases: orthorhombic polar phase at room temperature (RT) and monoclinic phase at high temperatures. The data about intermediate phases are extremely inconsistent. In this work the phase transitions peculiarities of BW and BM were investigated by mutual substitution Mo and W cations. Two series of $Bi_2W_{1-x}Mo_xO_6$ ($0 < x < 1$) ceramics have been synthesized at 600–630°C (**I**) and 850°C (**II**). X-ray powder diffraction at RT, differential scanning calorimetry, dielectric permittivity and conductivity measurements were used for phase identification and investigation of polymorphism. The samples of