

examine whether fabrication of SRG on the organic "single crystal" is possible or not by irradiation with two coherent laser beams. If possible, the study of photoinduced SRG formation using single crystals may provide information about not only the mechanism of the SRG formation but also the molecular motion near the surface of the organic crystal. In the present study, photoinduced SRG formation on an organic single crystal has been demonstrated by using 4-(dimethylamino)azobenzene. It was found that the SRG formation was greatly depending upon both the orientation of the crystal and the polarization of the writing beams. The dependence of the polarization of the writing beams on the SRG formation using the single crystal was found to be quite different from that reported for amorphous polymers and photochromic amorphous molecular materials.

Keywords: photochromism, surface morphology, materials science

### P08.04.15

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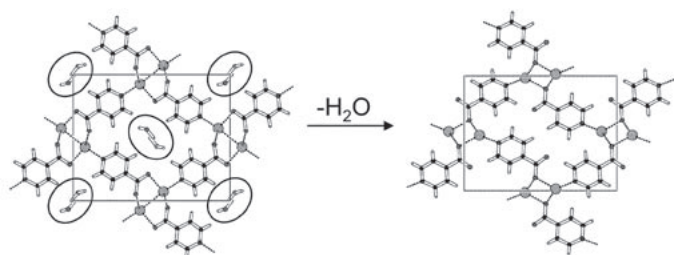
#### From crystal to crystal: Dehydration of (4-carboxylato)silver(I) monohydrate

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(4-carboxylato)silver(I) monohydrate was obtained via reaction of isonicotinic acid and silver carbonate. The resulting three-dimensional coordination polymer was described recently. [1] The left part of the figure shows a projection of the unit cell in which the water-containing voids have been highlighted. The solvent molecules do not strongly interact with the framework. Under vacuum the topotactic dehydration of this monohydrate to its unsolvated form (Figure, right) occurs. The reaction proceeds as single-crystal-to-single-crystal transformation and is irreversible. During the topotactic desolvation, the 3D framework transforms into a two-dimensional layer structure.

[1] W.-G. Lu, J.-Z. Gu, L. Jiang, C.-Y. Su, T.-B. Lu, *Chin. J. Inorg. Chem.*, 22, 1977 (2006).



Keywords: topochemistry, coordination polymer, single-crystal-to-single-crystal transformation

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#### Synthesis and characterization of $TAgM_3X_6$ (T = Mn, Fe; M = Sb, Bi; X = Se)

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Three new quaternary selenides  $TAgM_3X_6$  (T = Mn, Fe; M = Sb, Bi; X = Se) has been prepared by heating stoichiometric amounts of the constituent metals and selenium in evacuated silica tubes at 1023K. The crystal structures were determined by single-crystal X-ray diffraction and the compound crystallizes in  $Ag_3Bi_7S_{12}$  structure type with monoclinic space group  $C2/m$  (No. 12, Z = 4). This structure features two NaCl (311)-type slabs, which stack along *c*-axis. The transition metals Mn and Fe are essential element to synthesize these compounds. Theoretical studies performed on  $MnAgBi_3Se_6$  show that the material is a semiconductor, which has been confirmed by the electric conductivity measurements. Magnetic susceptibility measurements show that the  $MnAgBi_3Se_6$  materials exhibit temperature dependent paramagnetism and obey the Curie-Weiss law with high-spin state of  $Mn^{2+}$ , whereas  $FeAgBi_3Se_6$  does not. The optical band gaps are  $\sim 0.75$  eV that are estimated by diffuse reflectance measurements.

Keywords: solid-state chemistry, solid-state compounds, selenides

### P08.04.17

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#### Availability of solid-state polymerization of amino acid NCAs as compared with solution reactions

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In general, *N*-carboxy amino acid anhydrides (amino acid NCAs) have been polymerized in solutions to obtain high-molecular-weight polypeptides. As the solution polymerization of  $\gamma$ -benzyl-L-glutamate NCA (BLG NCA) has been extensively investigated, the reaction in dioxane, dichloromethane, etc. was compared with the solid-state polymerization. The solid-state polymerization was carried out by putting the NCA crystals into hexane which cannot dissolve the NCA and the polymer. Butyl amine was added as initiator. We found that the solid-state reaction was more reactive than the solution reaction, avoiding a moisture contamination (see Fig.1). The reactivity of NCA was affected by the purity of the NCAs. The polypeptides with monodisperse high-molecular-weight, which had not been prepared so far were obtained. Crystal structures of BLG, L-leucine and L-phenylalanine NCAs were found to be preferable for the polymerization in the solid state (see Fig.2). Polypeptides of alanine, valine, leucine, etc. which are not soluble in usual solvents can be prepared by the solid-state polymerization of the NCA. It is necessary to correct the misunderstanding concerning the reactivity of the NCAs.

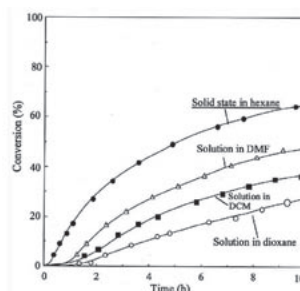


Fig.1 Time conversion curves of the polymerization of BLG NCA in the solid state in hexane and solutions at 30° C; M/I=200 and Cl content of NCA=0.0512 wt%.

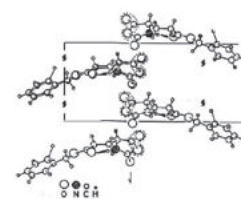


Fig.2 BLG NCA crystal (P212121)