

field  $E = 1 \text{ kV mm}^{-1}$ , the changes of bond length were  $(5.2 \pm 0.2)10^{-5} \text{ \AA}$  and  $(3.0 \pm 0.8)10^{-5} \text{ \AA}$ , respectively. The same measurements on  $\text{LiH}_2\text{PO}_3$  ( $a_1=11.024$ ,  $a_2=5.060$ ,  $a_3=5.169$ ,  $Z=4$ )[1] are under way and will be compared with the results of  $\text{LiH}_2\text{PO}_4$ . This will help to understand the relationship between external deformation and the specific response of chemical bonds in ternary compounds.

[1] S. Haussühl, *Cryst. Res. Technol.* 31, 1996, 323-327.

**Keywords:** piezoelectric, deformation, electric field.

## MS79.P14

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### Crystallographic analysis of $x\text{Li}_2\text{MnO}_3 \cdot (1-x)\text{LiMO}_2$ material for lithium batteries.

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In recent years layered compounds of the  $x\text{Li}_2\text{MnO}_3 \cdot (1-x)\text{Li(TM)O}_2$  series (TM = transition metal or a combination of transition metals with Mn  $x=0.3$ ; 0.5; 0.7) have been extensively studied as promising cathode materials for lithium-ion batteries. The  $\text{Li(TM)O}_2$  structural component adopts a layered  $\alpha\text{-NaFeO}_2$ -type structure (rhombohedral  $R\bar{3}m$  symmetry) in which the Na sites are occupied by Li, and the Fe sites are occupied by TM ions, thus forming alternating lithium layers and layers of transition metal separated by close-packed oxygen atomic planes. During the charge/discharge cycle, Li ions leave/fill their sites, while charge neutrality of the unit cell is preserved by oxidation/reduction of TM atoms. The second component,  $\text{Li}_2\text{MnO}_3$  (monoclinic,  $C2/m$ ), is also associated with the parent layered structure of  $\alpha\text{-NaFeO}_2$ : like in the rhombohedral  $\text{Li(TM)O}_2$  phase Li and Mn atoms occupy, respectively, Na and Fe sites in the  $\alpha\text{-NaFeO}_2$ -type structure, however excess Li atoms substitute for Mn at 1/3 of the atomic positions in Mn-planes.

The  $\text{Li}_2\text{MnO}_3$  compound is normally electrochemically inactive for lithium insertion and extraction, however, when synthesized in a nanocrystalline form it becomes electroactive, probably due to the factors associated with the material's defect chemistry, which is not well understood. Moreover, there is a subject for discussions in the literature whether the compounds  $x\text{Li}_2\text{MnO}_3 \cdot (1-x)\text{Li(TM)O}_2$  form homogeneous solid solutions or contain  $\text{Li}_2\text{MnO}_3$  domains within a  $\text{Li(TM)O}_2$  matrix. Thus, crystallographic structural studies of  $\text{Li}_2\text{MnO}_3$  are both of fundamental and technological interest.

In this study, we present our results of investigation of the structure of  $x\text{Li}_2\text{MnO}_3 \cdot (1-x)\text{Li}(\text{Mn}1/3\text{Ni}1/3\text{Co}1/3)\text{O}_2$  material by XRD, electron diffraction and high-resolution transmission electron microscopy techniques. The material was synthesized by a self-combustion reaction (SCR) using precursors of lithium nitrate, nickel (II) nitrate, manganese (II) nitrate, and cobalt (II) nitrate as oxidants and sucrose as the fuel.

On the basis of results Rietveld analysis of powder XRD patterns it was concluded that structure of this material consists of two components: the rhombohedral phase possessing the structure of  $\text{LiNiO}_2$  (space group  $R\bar{3}m$ ) and the monoclinic phase  $\text{Li}_2\text{MnO}_3$  described by space group  $C2/m$ . Varying the ratios of the Ni, Co and Mn occupancies on the nickel site in the  $\text{LiNiO}_2$  structure and varying Mn occupancy and Li/Mn ratio in sites  $4g$  and  $2b$ , respectively, in the  $\text{Li}_2\text{MnO}_3$  structure we obtained that in the  $\text{LiNiO}_2$  phase the lithium occupancy on the  $3b$  site is 100%. Hence, the lithium layer is not contaminated, and the Li/Mn ratio on the  $2b$  in  $\text{Li}_2\text{MnO}_3$  phase is about 5/4.

TEM examinations of  $x\text{Li}_2\text{MnO}_3 \cdot (1-x)\text{LiMn}1/3\text{Ni}1/3\text{Co}1/3\text{O}_2$  provided evidence that the material is comprised of nanodomains of

both rhombohedral  $\text{LiNiO}_2$ -like and monoclinic  $\text{Li}_2\text{MnO}_3$  structures, which are integrated and interconnected with one another at the atomic level. It was possible to distinguish between both components in high resolution micrographs.

**Keywords:** structural characteristics, TEM, cathode materials

## MS80.P01

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### Dynamic control of photochromic property in Salicylideneaniline hydrate crystals

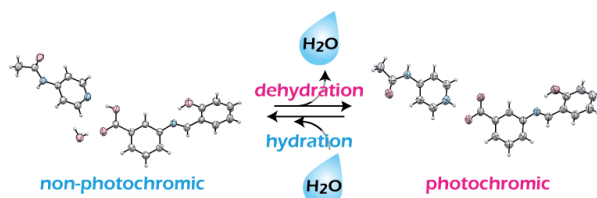
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Photochromism, light-induced reversible color change of substances, has attracted much attention due to its potential applications such as optical data storages, rewritable paper and biomolecular sensor etc. Salicylideneaniline (SA) derivatives are well-known solid-state photochromic substances that change the color from yellow to red by UV irradiation and red to yellow by visible light irradiation or heat. The yellow to red color change is explained as a tautomerism from the enol (yellow) to the cis-keto intermediate form followed by conformational change to the trans-keto form (red), which is cis-trans isomerization. In this study, we introduce the dynamic control of the photochromic property in SA hydrate crystals using hydration and dehydration process.

As a part of photochromic property control study by modifying molecular conformation and crystal environment<sup>1</sup>, some hydrated crystals were obtained. The crystal of *N*-salicylidene-4-carboxyaniline was a photochromic hemihydrate phase (**1a**). After heating, it was found that the hydrated phase has changed to a new dehydrated phase without photochromic property. In the crystal structure of the hydrated phase, the molecular structure of SA moiety had a non-planar conformation, the intra-molecular dihedral angle was 45 degrees. This result is in agreement with the knowledge that the non-planar SA derivative has a photochromic property. From these results, it is supposed that the dehydration process (pseudo-polymorphic transition) causes the conformational change from non-planar to planar of SA molecule due to the crystalline environment changes.

Meanwhile the co-crystal of *N*-salicylidene-3-carboxyaniline and 4-acetamidopyridine was obtained as a monohydrate crystalline phase (**2a**) showing no photochromism. However, under low-humidity condition or by heating, it transformed into new photochromic crystalline phase (**2b**) which was analyzed to be dehydrated. Reversibly this dehydrated phase (**2b**) turned to monohydrate phase (**2a**) by water vapor application and the photochromic property disappeared. This photochromism switching is explained by the change of intra-molecular dihedral angles in phases **2a** (27 degrees, non-photochromic) and **2b** (43 degrees, photochromic).

These results show that the photochromic property of SA is dynamically controlled by crystalline environmental change due to the hydration / dehydration processes and additionally in the **2a** and **2b** phases the photochromism switching property was realized.



Photochromism switching by hydration and dehydration processes

[1] K. Johmoto, A. Sekine, H. Uekusa and Y. Ohashi, *Bull. Chem. Soc. Jpn.* **2009**, *82*, *1*, 50-57.

**Keywords:** photochromism, control, hydration

## MS80.P02

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### Control of photochromic reactivity in hybrid type cobaloxime complex

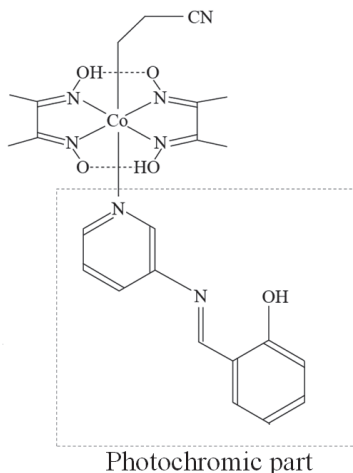
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Photochromic materials have attracted attention in recent years. One of our challenges in this field is to control the Photochromic reactivities of those materials. In order to create new materials that have dynamically controllable photochromic property, we designed new hybrid type cobaloxime complexes with photochromic compounds. In such crystals, photochromism is expected to change dynamically associating with crystalline-state photo-isomerization of cobaloxime complexes. In this study, (1) salicylideneaminopyridine (SAP) and (2) aminoazobenzene (AAB) derivatives are used as photochromic compounds, and the relationships between the structure dependent photochromic reactivity and isomerization reaction of cobaloxime complex in the crystalline state were investigated.

( $\beta$ -cyanoethyl)(*N*-(3,5-di-*tert*-butylsalicylidene)-3-aminopyridine)cobaloxime, (Co-SAP), and ( $\beta$ -cyanoethyl)(4-aminoazobenzene)cobaloxime, (Co-AAB), for (1) and (2), respectively, were successfully synthesized. Single crystal of Co-SAP was obtained from diethylether solution and the structure was characterized by single crystal X-ray diffraction analyses. The dihedral angle of phenyl rings of SAP is 45.28° and it has non-planer conformation, which means solid-state photochromic reaction is expected in SAP moiety. In the photoreactivity measurement of Co-SAP, the SAP moiety displayed the photochromism in the solid-state upon UV irradiation. After the photoisomerization of the cobaloxime moiety upon visible light irradiation, the photochromic property was examined to show the lifetime of colored species became significantly shorter than before reaction. It would be explained that the reaction cavity around the SAP moiety was modified by solid-state photoisomerization reaction of alkyl group of the cobaloxime complex, which successfully enabled the control of the photochromism.

The azobenzene derivative (AAB) shows no photochromic reaction in its crystalline-state as the trans-cis conformational change would not be allowed in confined crystalline environment. However, such photoreaction can be expected if the photo-isomerization of cobaloxime moiety loosens the reaction cavity around AAB moiety in Co-AAB. Actually, only after the photoisomerization reaction upon visible light irradiation on powdery crystals, the trans-cis type photochromism of AAB in solid-state was successfully observed for the first time, showing the hybrid cobaloxime complex strategy is so effective.

**Keywords:** photochromism, photoisomerization, solid state reaction



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### Photo-induced metastable low spin state in a iron(II) high spin complex

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Six-coordinated Fe(II) spin crossover compounds are commonly observed to undergo a light-induced low spin (LS) to metastable high spin (HS) transition through the LIESST phenomenon (Light-Induced Excited Spin-State Trapping). The generated metastable HS state is possible to transfer back to the LS ground state in the light irradiation of different wavelength through the reverse-LIESST procedure. Polymorph A of complex [Fe<sup>II</sup>(abpt)<sub>2</sub>(NCS)<sub>2</sub>] is known to undergo a temperature dependent spin transition with a LS ground state, and the observed LIESST phenomenon confirms the existence of low-lying metastable HS state. Polymorph B is reported to be a high spin complex in the studied temperature range 2-300 K, considering the same mononuclear molecule constitution but different packing crystal structure, a low-lying metastable LS state is expected and was studied by photocrystallographic, photomagnetic and light-induced FTIR experiments.

For thiocyanate-coordinating spin crossover complexes, the Fe-N bond length difference associated with HS and LS states makes the thiocyanate C≡N stretching frequency shifts significantly. The CN stretching frequency in the range of 1900-2200 cm<sup>-1</sup> is thus used to monitor the spin state change at various conditions. The light-induced FTIR experiment was accomplished with an 808 nm laser light source. By comparing the spectra before and after the laser treatment, the emerging absorption band at 2122 cm<sup>-1</sup> indicates the partial formation of metastable LS state. The photomagnetic measurement was also used to verify the metastable LS state. At 10 K, there is an abrupt drop in magnetic moment after 808 nm laser irradiation, which corresponds to a partial spin transition from HS (S=2) to metastable LS (S=0) state. When the sample is subsequently warmed up slowly in the dark, the magnetic moment raises gradually and meets the original cooling curve at temperature higher than 50 K (T<sub>LIESST</sub> (LS→HS) = 45 K). The metastable LS species induced by 808 nm laser below 45 K can also be excited to HS state via consecutive 532 nm laser treatment.

The photocrystallographic experiment was carried out at beamline BLB02B1 in SPring8, single crystal diffraction data sets were collected first in the dark and then on the continuous 808 nm laser irradiation at 25 K. With the space group remains unchanged and only minor difference observed in cell parameters, the intensity of some reflection did varied significantly after irradiation of 808 nm laser. The molecular structure for metastable LS was successfully extracted by introducing the fixed HS ground state one (in the dark) and refined using a disordered model. The site occupancy factor indicates 20 % of metastable LS component is formed, that is consistent with the photomagnetic experiment result. The Fe-N bond distances 2.060, 2.003, 1.972 Å for metastable LS is in agreement with the expected LS state configuration, while that of the HS ground state are 2.214, 2.160, 2.127 Å, respectively.

**Keywords:** photocrystallography, spin transition, metastable