

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-3m 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-3m) 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

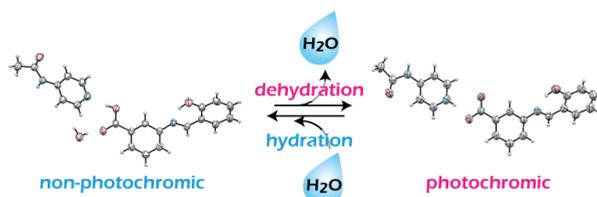
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Photochromism, light-induced reversible color change of substances, has attracted much attention due to its potential applications such as optical data storages, rewritable paper and biomolecular sensor etc. Salicylideneaniline (SA) derivatives are 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-acetamidepyridine 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