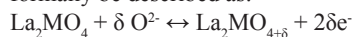


Scherrer Institute, Laboratory for Developments and Methods, 5232 Villigen PSI, Switzerland.

E-mail: juerg.schefer@psi.ch

The understanding of chemical reactivity of solids at low temperatures in terms of structural modifications and disorder occurring during the reaction process is still a relatively unknown and poorly understood field. Due to the strong applied character of this discipline this is a rather surprising fact, as this knowledge is necessary e.g. for the tailoring of new high-current and non-toxic battery systems; In this context we are interested to better understand the reaction mechanism of oxygen intercalation into solid oxides, i.e. oxides with K_2NiF_4 -type structure such as $La_2MO_{4+\delta}$ showing very high oxygen diffusion rates already present at low temperature which are therefore promising candidates for being used e.g. as oxygen membrane in solid oxide fuel cells. The reaction which can be performed in an aqueous alkaline electrolyte at ambient temperature can formally be described as:



Among this family of compounds La_2CoO_4 plays - due to the relatively high stability of Co^{3+} - a key role in terms of chemical reactivity as it shows with $\delta = 0.25$ the highest oxygen intercalation rate compared to Cu or Ni with a δ_{max} of 0.07 and 0.18 respectively. For stoichiometric $La_2CoO_{4.00}$ the same octahedral LTO (Low Temperature Orthorhombic) tilting arrangement as the one present for the isostructural La_2CuO_4 compound is observed at 293 K (space group Bmab), but small quantities of intercalated oxygen are sufficient to induce local lattice distortions as the extra oxygen atoms are located on interstitial sites [2]. Applying electrochemical oxidation we were, however, able to intercalate relatively high extra oxygen contents up to $\delta = 0.25$, which for $La_2CoO_{4.19}$ results in a 2D incommensurately modulated structure due to the ordering of the extra oxygen atoms, which at a stoichiometry of $La_2CoO_{4.25}$ shows a lock-in transition to a 2D commensurately modulated structure ($4a \times 4a \times c$ unit cell) which is directly related to the ordered distribution of the extra oxygen atoms. These two ordered phases show weak but sharp satellite or superstructure reflections up to high $\sin\theta/\lambda$ values which are completely unexpected as the reaction performs at 293 K i.e. far away from thermal equilibrium where complete relaxation of lattice hindered (see Fig 1).

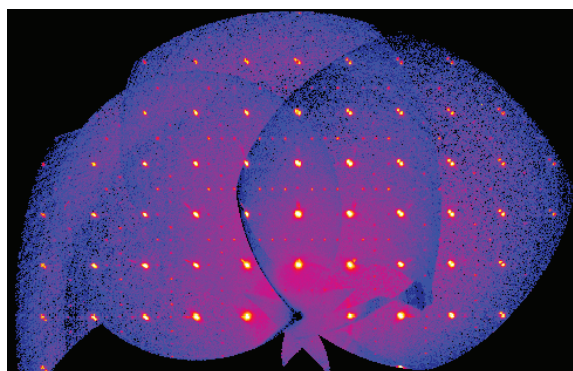


Fig. 1 Section of the (hk1) diffraction plane obtained on an electrochemically oxidized single-crystal by laboratory X-ray

diffraction with the use of a CCD detector. The sharp superstructure reflections of the twinned crystal correspond to a $4a \times 4a \times c$ unit cell.

This electrochemically induced ordering of the extra oxygen atoms also strongly influences the physical properties of $La_2CoO_{4.25}$ as antiferromagnetic ordering is observed below 35K, whereas all disordered phases do not show any magnetic ordering.

$La_2CoO_{4.25}$ contains equivalent amount of Co^{2+} and Co^{3+} (the latter is non-magnetic in the low spin state) and the interstitial oxygen stoichiometry correspond to one extra oxygen atom per unit cell. This gives a complex scenario between charge separation, magnetic ordering and long range ordering of interstitial oxygen atoms which crucial for the interpretation of the chemical reactivity and the physical properties of these compounds.

[1] W. Paulus *et al.* *Solid State Sciences* 4, **2001**, 565. [2] R. Le Toquin, W. Paulus^a, A. Cousson, G. Dhalenne, A. Revcolevschi, *Physica B* 350, **2004**, 269. [3] J.M. Tranquada, *J. Phys. Chem. Solids* 59, **1998**, 2150 ; *Nature*, 375, **1995**, 561.

FA4-MS05-P44

Synthesis, Spectroscopic and Structural Characterization Of Bis(Benzimidazole- κN^3) Bis(2-Benzoylbenzoato- κO)Copper(II).

Zerrin Heren^a, Hümeýra Paşaođlu^b, M. Hakkı Yıldırım^b.

^aOndokuz Mayıs University Faculty of Arts and Sciences Department of Chemistry, Samsun, Turkey.

^bOndokuz Mayıs University Faculty of Arts and Sciences Department of Physics, Samsun, Turkey.

E-mail: zheren@omu.edu.tr

A novel Cu^{II} complex of the 2-benzoylbenzoato ligand (2-byba) with benzimidazole (bim) was synthesized and characterized by elemental analysis, FT-IR spectroscopy, and X-ray diffraction. In the complex, the Cu^{II} ion lying on a centre of symmetry, is in a square-planar coordination geometry formed by two symmetry related 2-byba and two symmetry related bim ligands (Fig. 1). Both ligands are monodentate with 2-byba coordinates carboxylate O atom and bim coordinates through the aromatic N atom. The molecular packing is mainly stabilized by strong intermolecular $N-H\cdots O$ hydrogen bonds. The FT-IR spectra of the complex is also discussed.

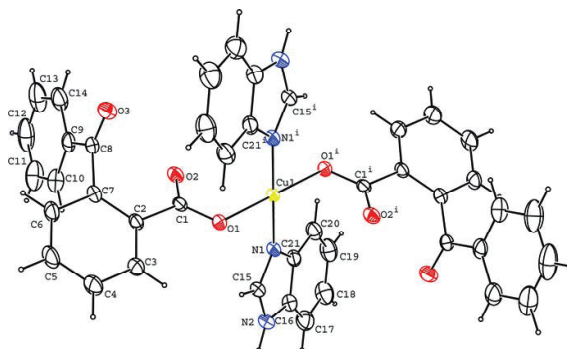


Fig. 1. The molecular structure of the complex.

Keywords: X-ray; benzimidazole; 2-benzoylbenzoate copper complex

FA4-MS05-P45

Synthesis, Spectrothermal and Structural Characterization of Saccharinatobis(tris-hydroxymethylaminomethane)zinc(II) saccharinate Complex, [Zn(sac)(tham)₂](sac).
Hümeýra Pasaoglu^a, Zerrin Heren^b, Gokhan Kastas^a, Kamber Akdag^a.^aDepartment of Physics, Faculty of Arts and Sciences, Ondokuz Mayıs University, Samsun, Turkey. ^bDepartment of Chemistry, Faculty of Arts and Sciences, Ondokuz Mayıs University, Samsun, Turkey.

E-mail: hpasa@omu.edu.tr

A novel Zn^{II} complex of the saccharinate ligand (sac) with tris-hydroxymethylaminomethane (tham) was synthesized and characterized by elemental analysis, FT-IR spectroscopy, simultaneous TG and DTA techniques, and X-ray diffraction. The complex, [Zn(sac)(tham)₂](sac), crystallizes in monoclinic system with space group P21/c [*a* = 7.55954(3) Å, *b* = 13.0532(6) Å, *c* = 27.7777(10) Å, β = 100.539(3)°, *Z* = 4]. The Zn^{II} ion has a distorted octahedral coordination. The tham ligand has chemically different functions in the structure, acting as both bidentate and tridentate ligands. There are also sac moieties to act as N-bonded ligand and as a counter anion. The molecular packing of the complex is provided by moderate hydrogen bonds as well as π···π interactions between the sac moieties. The IR spectra and the thermal decomposition of the complex are also discussed.

Keywords: zinc; saccharinato complex; tris-hydroxymethylaminomethane; crystal structure; thermal decomposition