

## METAL-ORGANIC FRAMEWORKS CONTAINING DIACETATES: POLYMORPHISM AND RELATED COMPOUNDS

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A systematic structural study of metal-organic frameworks (MOFs) based on oxydiacetate (oda) organic ligand, lanthanoid (Ln) and divalent 3d or alkaline-earth (M) cations with general formula  $[\text{Ln}_2\text{M}_3(\text{oda})_6(\text{H}_2\text{O})_6] \cdot x\text{H}_2\text{O}$  is being carried out with the aim of understanding the interesting magnetic and gas-storage properties observed in the system [1,2]. Compounds prepared as previously described [1-4] are being structurally characterized by x-ray powder diffraction using the in-house Rigaku ULTIMA IV powder diffractometer and the instrument at 11BM-B station at the Advanced Photon Source at Argonne National Laboratory.

Two polymorphs with general formula  $[\text{Ln}_2\text{M}_3(\text{oda})_6(\text{H}_2\text{O})_6] \cdot x\text{H}_2\text{O}$  have been described so far. An hexagonal form (H, S.G. P6/mcc) mainly observed for M=Cu, Ni and in some cases Co where the Ln and M ligand form an open framework where ~11 Å diameter channels are observed and cubic form (C, S.G. Fd3c) that is better described as  $[\{\text{M}(\text{H}_2\text{O})_6\}\{\text{LnM}(\text{oda})_3\}_2] \cdot x\text{H}_2\text{O}$  where two inequivalent M cations exist (more frequently Mg, Ca, Mn and sometimes Co) 2/3 forming a 3D anionic network with Ln and oda and 1/3 hexaaquo cations occupying the voids in an ordered manner. H form with Ln=Sm and M=Co has been shown to be able to store up to 1.2%w H<sub>2</sub> at 77 K [2] after water removal while C form with Ln=Gd and M=Mn shows a ferromagnetic coupling among in-network Gd<sup>3+</sup> and Mn<sup>2+</sup> magnetic cations below 25 K. For samples with LnM combinations SmMn, GdMn, YbMn and YbCo a trigonal (T), pseudo-cubic structure is found in the fresh precipitate that evolves to the C form during diffraction data collection (irradiation) or heat treatment. An additional monomeric form with formula  $(\text{NH}_4)[\text{M}(\text{H}_2\text{O})_6][\text{Ln}(\text{oda})_3] \cdot x\text{H}_2\text{O}$  is frequently obtained as precipitate instead of the H and C MOFs for the Ln-M combinations where these forms are not favoured (N: S.G. P2<sub>1</sub>/n for Ln=Yb, or P-1 otherwise).

In this poster we will show the structural results obtained for GdCa, YbCa, GdMn and YbCo samples showing C, C, T/C and N/T/C phases respectively obtained from Rietveld refinement of synchrotron and conventional x-ray powder diffraction data.

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