

NEW OPEN FRAMEWORK INDIUM-BASED METAL ORGANIC FRAMEWORK MATERIAL: SYNTHESIS AND CRYSTAL STRUCTURE DESCRIPTION

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ABSTRACT

A new MOF-type indium pyromellitate (MIL-117) was hydrothermally synthesized at 483 K for 24 hours. The structure of MIL-117 with formula $\text{In}_6(\text{OH})_6(\text{btec})_4 \cdot 9\text{H}_2\text{O}$ (btec = 1,2,4,5-benzenetetracarboxylate) has orthorhombic (*Pnmm*) symmetry and unit cell parameters $a = 8.2390(8)$, $b = 22.251(2)$, $c = 37.791(4)$ Å, $V = 6928.2(11)$ Å³. It contains 3-D open framework of infinite chains of unusual *cis* sharing In-centered octahedra linked to each other through the pyromellitate ligands. The three distinct In(III) cations are coordinated with four oxygen atoms from carboxyl groups and two μ_2 -hydroxyl groups in *cis* positions. The MIL-117 network delimits one-dimensional channels of 7.7 x 8.0 Å running along the *a* axis, where occluded water molecules are located. Although water species can be easily removed from the pore, no N₂ sorption was observed at 77 K for its BET surface area estimation.

Keywords: hydrothermal synthesis; metal-organic framework; indium; pyromellitate.

INTRODUCTION

Metal-organic framework materials (MOFs) exhibit immense potential applications such as catalysis [1], gas storage and separations [2,3] and drug delivery [4] particularly due to the possibility to design their porous framework structure. Combination of aromatic polycarboxylic acids (such as 1,4-benzenedicarboxylic, 2,6-naphthalenedicarboxylic, 1,3,5-benzenetricarboxylic, 1,2,4,5-benzenetetracarboxylic acid) with divalent metal precursors (Zn, Cu, Co, Cd, etc.) resulted in numerous three-dimensional structures with promising porous properties. Indium-based carboxylates display different network topologies, mainly due to the variety of coordination (VI, VII or VIII) with O-ligands. [5, 6] Moreover, some of them exhibit good catalytic, ion-exchange, hydrogen storage or fluorescence properties [7-9].

Here, we report on the synthesis and structural characterization of new indium-based pyromellitate $\text{In}_6(\text{OH})_6(\text{btec})_4 \cdot 9\text{H}_2\text{O}$ (called MIL-117) with a three-dimensional open framework containing infinite chains of *cis*-connected $\text{InO}_4(\text{OH})_2$ octahedra linked with the tetradentate ligand btec.

EXPERIMENTAL

Indium pyromellitate or MIL-117 was hydrothermally synthesized under autogenous pressure from mixture of elemental indium (In, Aldrich, 99.99%), 1,2,4,5-benzenetetracarboxylic acid ($\text{C}_6\text{H}_2(\text{CO}_2\text{H})_4$ or btec, Aldrich, 96%) and distilled water with the following molar ratios 1 : 0.1 : 140. MIL-117 phase is formed only from reaction mixtures with very restrict In/H₄btec molar ratios and low yield (30 %) with the respect to In. When the amount of pyromellitic acid is increased in the reaction mixture, the phase $\text{In}(\text{OH})(\text{H}_2\text{btec}) \cdot \text{H}_2\text{O}$ is formed, whereas decreased acid amount results in the formation of the product with major amount of unreacted In metal. Starting reagents (In: 220 mg, 2 mmol; H₄btec: 50 mg, 0.2 mmol; H₂O: 5 ml, 278 mmol) were placed into 23 ml autoclave and treated at 483 K for 24 hours. Longer crystallization times led to the non-pure products. pH

value remained 2 during the crystallization process. Obtained thin plate-like crystals were continuously rinsed with distilled water and dried at room temperature.

Single-crystal X-ray diffraction. The intensity data were recorded on a Siemens SMART three-circle diffractometer equipped with a CCD bidimensional detector using Mo- K_{α} radiation ($\lambda = 0.71073 \text{ \AA}$). The structure was solved by direct methods and refined by full-matrix least squares on F^2 using the SHELXTL package. All the non-hydrogen atoms (except water molecules) were refined with anisotropic thermal parameters. H atoms bonded to C were placed using geometrical constraints.

Thermogravimetric analysis. The thermal analysis (TG/DTG) was performed on a SDT 2960 Thermal Analysis System (TA Instruments, Inc.). The measurements were carried out in static air Elmer, with the heating rate 10 K/min.

Thermodiffraction. Structural changes during the heating were investigated on a PANalytical X'Pert PRO high-resolution diffractometer with Cu $K_{\alpha 1}$ radiation ($\lambda = 1.5406 \text{ \AA}$) in the range from 4 to 60 ° 2 θ using step of 0.034 ° per 100 s. Diffraction patterns were recorded every 50 K from room temperature to 773 K in air.

RESULTS AND DISCUSSION

Structure description. The three-dimensional structure of MIL-117 consists of infinite chains octahedrally coordinated indium cations linked to each through the pyromellitate linker via the carboxylates linkers (Figure 1). There exist three distinct crystallographic sites for indium (In1, In2, In3), which are bonded to four oxygen atoms coming from carboxylate groups and two hydroxo groups. For In1 and In2, two of the carboxyl oxygens belong to carboxylate groups having a *syn-syn* bidentate mode bridging two adjacent indium cations and the two others belong to carboxylate having a *syn* terminal monodentate mode. In3 cation is connected to four carboxyl oxygens from carboxylate groups with only the *syn-syn* bidentate mode. The two remaining oxygen atoms bonded to indium correspond to hydroxo groups (O2, O3, O5) and are shared between two indium atoms (μ_2 -). The positions of the two μ_2 -OH species are quite unusual within the InO₄(OH)₂ octahedral surrounding since they are located with a *cis* configuration. It results in the formation of infinite chains with the InO₄(OH)₂ octahedra connected to each other *via* μ_2 -OH, with the sequence "...In1-OH-In2-OH-In3...". This zigzag chain induced by the *cis* connection mode is developed along the *a* axis. This feature is unique since straight chains of *trans*-connected octahedra are commonly observed in the other carboxylates with six-fold coordinated indium or other series of metal carboxylates.

The chains are then connected to each other through pyromellitate ligands. One distinguishes four distinct crystallographic organic linkers, which are all located along a mirror plane along the C-H axis of the benzene ring. The first type of pyromellitate species connects two distinct inorganic chains along the (*a,c*) plane and acts as a bidentate linker through all the carboxylate functions. Along the perpendicular (*a,b*) plane, the chains are linked to each other through two types of pyromellitate anions which are connected to indium atoms in a same manner through the carboxylates with bidentate and monodentate fashions. This type of connection generates square-shape tunnels with an estimated free diameter of 7.7 x 8.0 Å running along the *a* axis and stacked along the *b* axis.

Thermal behavior. Thermogravimetric analysis curve given on Figure 2 a shows two major weight losses. The first weight loss of 13.0 wt% up to 453 K is attributed to the removal of physisorbed water. Theoretical water loss calculated from the chemical formula In₆(OH)₆(btec)₃(H₄btec)·9H₂O is 8.3 wt%, which implies that there is approximately 5 wt% of additional water adsorbed on the surface or trapped within the pores. The second weight loss of 42.1 wt%, performed in two steps, between 573 and 793 K indicates the decomposition of

benzenetetracarboxylate ligand and removal of its fragments. The final residue of 44.9 wt% (calc.: 42.6 wt%) corresponds to indium oxide In_2O_3 .

X-ray thermodiffraction analysis (Figure 2 b) shows two structural changes. First change occurs at 373 K and most probably corresponds to a small structural rearrangement due to the water removal. Dehydrated MIL-117 remains stable up to 673 K where intensity of peaks decreases due to the framework decomposition process leading to the formation of In_2O_3 upon further heating. In order to investigate reversibility of hydration/dehydration process, high-temperature form of MIL-117 heated at 423 K, was exposed to the controlled atmosphere with 85 % of humidity at ambient temperature overnight. The XRD patterns of as-synthesized, dehydrated (heated) and re-hydrated samples of MIL-117 are shown in Fig. 3. XRD pattern of dehydrated sample indicates that structural change occurs as regards to as-synthesized sample. Re-hydration causes structural rearrangement back into as-synthesized form; however, the intensity of the reflections is decreased in comparison with starting material. This investigation indicates that process of MIL-117 dehydration/rehydration is reversible. However, adsorption experiment involving nitrogen at 77 K for the determination of potential BET surface area did not lead to any uptake.

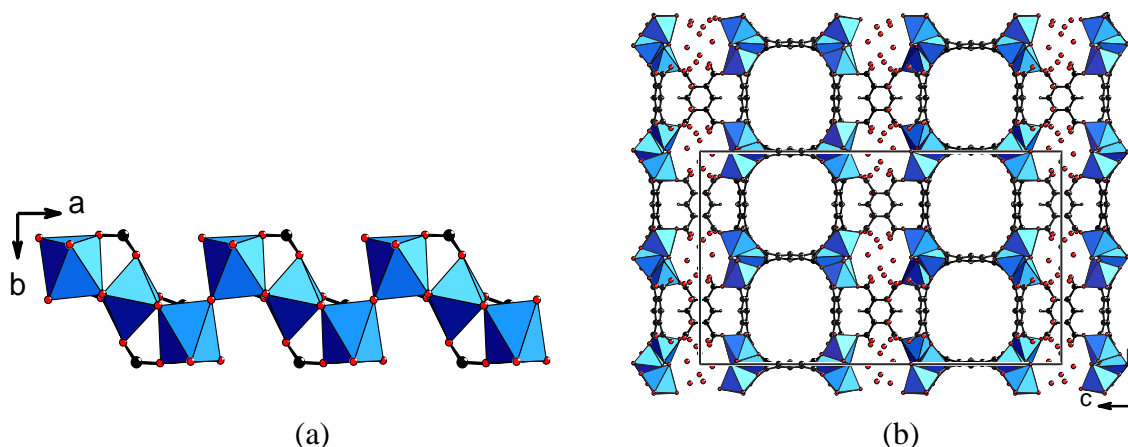


Figure 1: (a) View of one chain of InO_6 octahedra (In1-In2-In3 alternation) running along the a axis, with the *cis* connection mode *via* the μ_2 -hydroxo groups. (b) View of the structure of MIL-117 showing the channels along the a axis. Blue octahedra: $\text{InO}_4(\text{OH})_2$; black circles: carbon; red circles: oxygen.

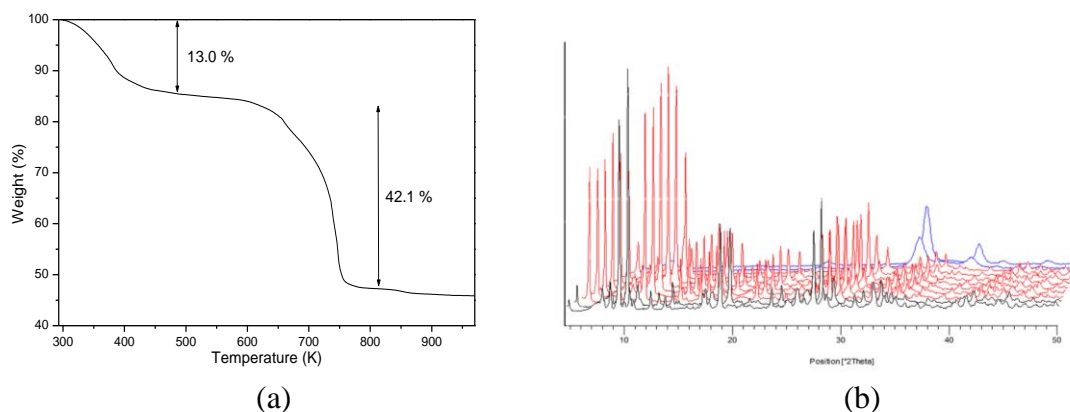


Figure 2: (a) TG curve of MIL-117 under air atmosphere. (b) Thermodiffraction patterns of MIL-117 from room temperature to 323 K (blue), from 373 to 523 K (red) and from 573 to 773 K (black).

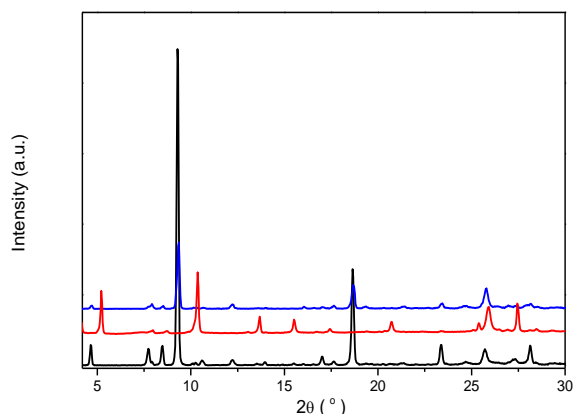


Figure 3: XRD powder patterns of MIL-117: as-synthesized (black), high-temperature form heated at 423 K (red), rehydrated (blue).

CONCLUSION

MIL-117 is crystallized by hydrothermal reaction between elemental indium and pyromellitic acid in aqueous medium. The three-dimensional framework is built from infinite corner-sharing $\text{InO}_4(\text{OH})_2$ octahedra connected through pyromellitate ligands. Octahedra are connected to each other *via* $\mu_2\text{-OH}$, with the sequence “In1-OH-In2-OH-In3” in the *cis* connection mode creating zigzag chains along *a* axis. Such an arrangement of octahedra is quite unique for six-fold coordinated indium polycarboxylates since occurrence of *trans*-connected octahedra with straight chains are commonly observed in indium-based carboxylate structures. Inorganic chains and benzene rings form pores with estimated free diameter of 7.7 x 8.0 Å in MIL-117. This material undergoes to a structural rearrangement upon heating at 373 K due to the water removal. Dehydrated (high-temperature) form of MIL-117 structure remains stable up to 673 K. When sample is rehydrated, the structure rearranges back to the as-synthesized form, confirming reversibility of dehydration/rehydration process.

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