

**MS15-P19** Two polymorphic nanoribbon structures with near-white light photoluminescenceSue-Lein Wang<sup>1</sup>

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Two polymorphic nanoribbon structures in the zincophosphate system (NTHU-14) were prepared and discovered to exhibit interesting photoluminescence (PL) properties. They are the first neutral organo-zinc phosphites in which the 2.8 nm-wide and S-shaped ribbons are arranged into R- and L- arrays, resulting in RLR and RRR stackings, thus creating two polymorphic phases: 14-alpha and 14-beta. Although both can display near-white light under the excitation of 320 nm UV-light, the two polymorphs reveal distinctly different emissions in the visible region. However, the major differences observed in optical property could not be ascribed to the difference in their structural as usually expected. We noted that for either R-arrays or L-arrays, pi-pi bonding is the only intra-array interaction force and hydrogen bonds is the only inter-array force, existing between a pair of adjacent ribbon arrays. Therefore, the two polymorphic structures are considered identical in terms of intra- and inter-ribbon-bonding interactions. In this presentation, descriptions and discussions on the synthetic strategy, the unique structures, characterizations, and the origin of emissions and the resultant photoluminescence properties for the two polymorphs of NTHU-14 are presented in detail.

**Keywords:** polymorph, photoluminescence, organo-zinc phosphite**MS15-P20** Novel ammonium manganese hydrate phosphate – a possible precursor for Li-ion batteriesGalina V. Kiriukhina<sup>1</sup>, Olga V. Yakubovich<sup>1,2</sup>, Olga V. Dimitrova<sup>1</sup>

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The crystal structure of a new modification of the niahite mineral  $\text{NH}_4\text{MnPO}_4 \cdot \text{H}_2\text{O}$ , obtained in the form of single crystals under hydrothermal conditions, is determined by X-ray diffraction (Xcalibur-S-CCD diffractometer,  $R = 0.0259$ ):  $a = 17.582$ ,  $b = 4.909$ , and  $c = 5.731$  Å; space group =  $Pnam$ ,  $Z = 4$ ,  $D_x = 2.497$  g/cm<sup>3</sup> [1].

A new modification of the niahite is centrosymmetric. Both structures are based on chess-board type layers built from  $\text{MnO}_6$  octahedra sharing O vertices.  $\text{PO}_4$  tetrahedra are attached to the free cages from both sides of these layers; the “hanging” vertex of the phosphate tetrahedra, which is unshared with other polyhedra, protrudes to the adjacent layer.  $\text{NH}_4$  groups are situated between the layers and form hydrogen bonds connecting the layers together.

As we showed earlier [2, 3], the niahite,  $\text{NH}_4\text{MnPO}_4 \cdot \text{H}_2\text{O}$  structure type can be obtained by the transformation of the crystal structure of lithiophilite  $\text{LiMnPO}_4$  (Fig. 1). The Mn/P layers of the same topology are repetitive polysomes of both crystal structures. These layers are directly connected into a 3D framework by sharing oxygen vertices of octahedra and tetrahedra. Small octahedral voids of the lithiophilite crystal structure are populated by Li atoms.

Olivine-type  $\text{LiMPO}_4$  ( $M = \text{Fe}, \text{Mn}, \text{Co}, \text{Ni}$ ) phosphates are currently among the most efficient cathode materials for lithium batteries [4–6]. In [4] it was shown that the  $\text{LiFePO}_4/\text{C}$ , which was synthesized, using the  $\text{NH}_4\text{FePO}_4 \cdot \text{H}_2\text{O}$  precursor, exhibits high rate capability at different current rate values. The  $\text{LiMnPO}_4/\text{C}$ , synthesized by the same procedure with the  $\text{NH}_4\text{MnPO}_4 \cdot \text{H}_2\text{O}$  precursor, exhibits sound, but lower with respect to the  $\text{LiFePO}_4/\text{C}$ , electrochemical properties [4–6]. This way of  $\text{LiMPO}_4$  phases' preparation is targeted to increase the capacity of the material. It was shown that synthesis of  $\text{LiMnPO}_4$  by ion exchange in the  $\text{NH}_4\text{MnPO}_4 \cdot \text{H}_2\text{O}$  precursor retains the morphology of precursor crystals. It is highly probable that the new centrosymmetric modification of “niahite” will be even more efficient for this purpose.

[1] G. Kiriukhina, O. Yakubovich, O. Dimitrova, Cryst. Rep. 60 (2), 198 (2015).

[2] O. Yakubovich, O. Karimova *et al.*, Acta Cryst. C 55, 151 (1999).