

Crystallography of Lithiated and Delithiated Transition Metal Phosphates and Thiophosphates

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Lithium transition metal phosphates and thiophosphates have been utilized in an endless amount of applications. The phosphates have been studied in magnetoelectrics, batteries, and quantum materials. We are specifically studying the phosphates to broaden the current understanding of ferrotoroidics. Similar to the well-known types of ferroic orders, ferrotoroidics undergo a spontaneous, physical change below a critical temperature. In this case, the spontaneous change is an alignment of toroidal moments [1]. Transition metal thiophosphates on the other hand are interesting 2D magnetic materials that have unique functionality that can be used in microelectronic, spintronic, and magnetoelectric applications [2]. These materials are crucial for moving past current limitations in computer technology. Magnetoelectric and spintronic devices are predicted to have numerous breakthroughs in data processing speeds, high storage density, and efficient energy consumption [3].

Due to their practical and important applications, the purpose of this research is to further support and expand the current understanding of both the phosphate and thiophosphate materials. This research is focused on two materials: $\text{Li}_{1-y}\text{Fe}_x\text{Mn}_{1-x}\text{PO}_4$, and $\text{Li}_2\text{MP}_2\text{S}_6$, where $M = \text{Fe}, \text{Co}$. While these two materials appear to be similar in some regards, we notice many differences as we dive deeper into the crystallography and magnetic behavior of these compounds.

The $\text{Li}_{1-y}\text{Fe}_x\text{Mn}_{1-x}\text{PO}_4$ materials have an orthorhombic Pnma crystal structure; the structure can be seen in the figure attached. This work focuses on the effect of partially delithiating this solid solution series. It is known that when the lithium is removed, the antiferromagnetic transition temperature (TN) increases significantly. While an increase in TN is promising, the problem with fully removing lithium from the lattice, is that there is a complete phase change. This new magnetic space group is slightly distorted and the magnetic moments are canted, removing the possibility of this material being a potential ferrotoroidic. The specific aim of this study is to determine how much lithium can be removed before this phase change occurs.

We have synthesized the entire phase pure $\text{Li}_{1-y}\text{Fe}_x\text{Mn}_{1-x}\text{PO}_4$ powder and single crystal series for analysis. We have used x-ray diffraction, neutron powder diffraction, ICP-AES, and SQUID magnetometry to better understand the nuclear and magnetic properties of these materials. We have found that even when you remove a small amount of lithium, TN increases without affecting the nuclear structure or the magnetic point group. We are in the final stages of analyzing the structural and magnetic properties of the entire lithiated and delithiated $\text{Li}_{1-y}\text{Fe}_x\text{Mn}_{1-x}\text{PO}_4$ series. We will soon be able to identify the maximum amount of lithium that can be removed while maintaining the original phase.

The second group of materials that we are looking at is the lithium transition metal thiophosphates of the formula $\text{Li}_2\text{MP}_2\text{S}_6$, where $M = \text{Fe}, \text{Co}$. The structure of $\text{Li}_2\text{FeP}_2\text{S}_6$ has been previously studied by Takada et al. using x-ray diffraction [4]. To the best of our knowledge, no magnetic properties of this material have been studied. In addition, neither the structural nor magnetic properties have been reported for the cobalt analog.

Phase pure powders and 4-6 mm long single crystals of both $\text{Li}_2\text{FeP}_2\text{S}_6$ and $\text{Li}_2\text{CoP}_2\text{S}_6$ have been synthesized via a solid-state method. The crystal structure of $\text{Li}_2\text{FeP}_2\text{S}_6$ reported by Takada et al. was confirmed using single crystal x-ray diffraction. The crystal structure of $\text{Li}_2\text{CoP}_2\text{S}_6$, which has not been published, was also determined using the single crystal xrd. The trigonal $\text{P}\bar{3}1\text{m}$ crystal structure can be seen in the figure attached. While isostructural in some regard, there are some crucial differences between these materials. First, the site occupancies are different, resulting in interesting charge balance conclusions. Secondly, there is a thiophosphate distortion as can be seen by the close up of the unit cell.

Originally, we chose these materials because their nuclear structure could potentially host long-range antiferromagnetic order. To our surprise, magnetic susceptibility and field dependent measurements demonstrated paramagnetic behavior for both the iron and the cobalt sample down to 2 K. This result was further confirmed by a lack of magnetic reflections in the time-of-flight neutron powder diffraction data. In contrast to their delithiated counterparts, these materials do not demonstrate any long-range magnetic order.

While the phosphates and the thiophosphates demonstrated very different structural and magnetic results, they both remain relevant materials for magnetoelectrics, ferrotoroidics, spintronics, quantum materials, and much more.

[1] Schmid, H. *Ferroelectrics* 2001, 252, 41-50. [2] McGuire, M. *Chemistry of Materials* 2015, 27. [4] Susner, M. A. *Advanced Materials* 2017. [5] Takada, K.; Tabuchi, M. *Solid State Ion* 2003, 15

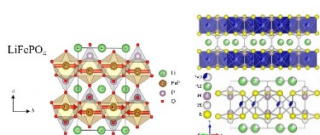


Figure 1

Figure 2