

Vibrational Spectroscopic Investigation of Li Extraction from Monoclinic and Rhombohedral $\text{Li}_3\text{V}_2(\text{PO}_4)_3$

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Introduction

The $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ family of compounds has generated interest as new cathode materials because of their high theoretical capacity. Most investigations of this family have focused on the monoclinic (α -) and rhombohedral (β -) forms of $\text{Li}_3\text{V}_2(\text{PO}_4)_3$.^{1,2} In β - $\text{Li}_3\text{V}_2(\text{PO}_4)_3$, two Li^+ ions may be reversibly extracted along a flat 3.7 V plateau, while all three lithium ions have been removed from α - $\text{Li}_3\text{V}_2(\text{PO}_4)_3$.

Extensive X-ray and neutron diffraction and $^7\text{Li}/^6\text{Li}$ NMR experiments have been conducted on α - and β - $\text{Li}_3\text{V}_2(\text{PO}_4)_3$.^{3,4} However, there have been no Raman or infrared spectroscopic studies of these compounds as a function of Li^+ content. Here we report vibrational spectroscopic studies of α - and β - $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ at various states of charge. Vibrational spectroscopic studies of LiFePO_4 clearly show changes in the intramolecular PO_4^{3-} vibrations when Li^+ ions are removed.⁵ Similarly, we expect the PO_4^{3-} anions in α - and β - $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ to be sensitive to Li^+ ion extraction. The ability to contrast structurally different forms of $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ is particularly valuable to gain insight into the electrochemistry of these materials.

Experimental Methods

The α - $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ was synthesized from stoichiometric amounts of Li_2CO_3 , V_2O_5 , and $\text{NH}_4\text{H}_2\text{PO}_4$. The precursors were ball-milled in acetone overnight. After the acetone evaporated, the mixture was heated at 300°C for 1h under a 10% H_2 -90% N_2 atmosphere to decompose the organic constituents. This was followed by an 18h thermal treatment at 900°C under the same atmosphere. The β - $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ was prepared by ion exchange from rhombohedral $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ (10 fold molar excess of LiNO_3). The procedure to prepare $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ was identical to that of α - $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ except Na_2CO_3 was substituted for Li_2CO_3 .

Electrodes were prepared by mixing the appropriate active material with KS-6 graphite, Timcal (5 wt%); Super P, 3M (5 wt%); and Teflon (3 wt%). Size 2430 coin cells were constructed using Li metal anodes and 1 M LiPF_6 dissolved in (1:1) EC-DMC as the electrolyte. Cells were cycled at 0.10 mA/cm^2 with an Arbin battery cycler. Afterwards, the electrodes were extracted, washed twice in DMC, and dried under reduced pressure at 50°C . Mid- and far-IR spectra were recorded on a Bruker IFS 66v spectrometer using KBr and CsI pellet techniques. Raman spectra were collected with a Jobin-Yvon ISA T64000 spectrometer. A 532 nm excitation laser ($\sim 5 \text{ mW}$) was focused onto the electrodes through a microscope. Each spectrum consists of a 60 min acquisition to increase the signal to noise ratio.

Preliminary Data

Preliminary infrared spectra of α - and β - $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ as a function of Li content are presented in Figs. 1 and 2, respectively. Numerous changes in the PO_4^{3-} stretching and bending modes result from the extraction of Li from α - $\text{Li}_3\text{V}_2(\text{PO}_4)_3$. Delithiation to α - $\text{Li}_1\text{V}_2(\text{PO}_4)_3$ produces

new bands at 1172 , 920 , and 853 cm^{-1} . However, extracting all the Li^+ ions results in the complete destruction of the PO_4^{3-} vibrational multiplet structure and results in broad bands for $\nu(\text{P-O})$ and $\delta(\text{O-P-O})$.² Removing Li^+ ions from β - $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ causes the $\nu(\text{P-O})$ modes to collapse into a large band centered at 1000 cm^{-1} . In contrast to the α - $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ system, the vibrational structure of β - $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ is not degraded when the maximum amount of Li is deintercalated. This is evidenced by the sharpness of the β - $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ bands at 560 , 577 , and 633 cm^{-1} compared to the broad α - $\text{V}_2(\text{PO}_4)_3$ band at 596 cm^{-1} .

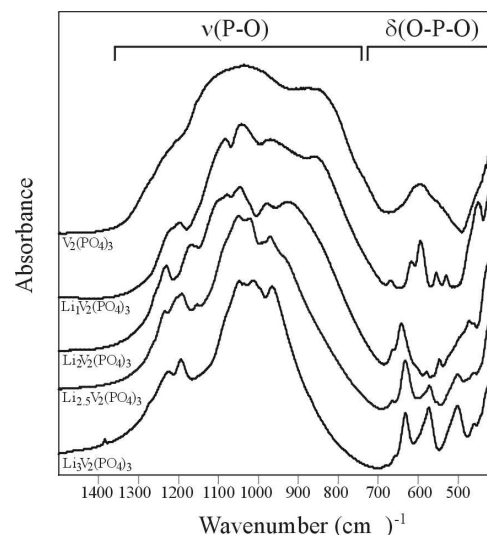


Fig. 1: Mid-IR spectra of α - $\text{Li}_x\text{V}_2(\text{PO}_4)_3$ where $x = 3.0, 2.5, 2.0, 1.0,$ and 0.0 .

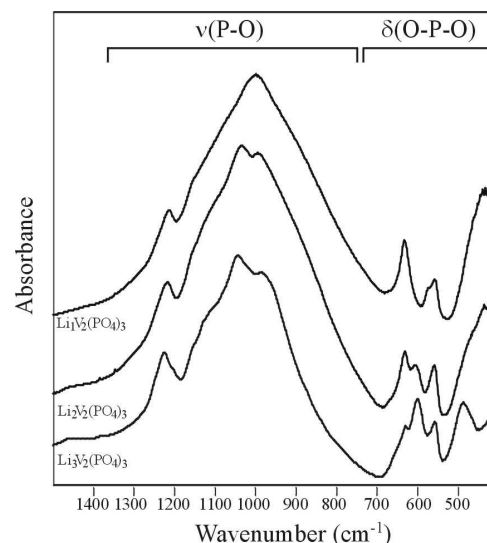


Fig. 2: Mid-IR spectra of β - $\text{Li}_x\text{V}_2(\text{PO}_4)_3$ where $x = 3.0, 2.0,$ and 1.0 .

References

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