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Raman Spectroscopy of LiFePO_4 and $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ Prepared as Cathode Materials

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Structure of samples of lithium iron vanadium phosphates of different compositions were investigated by X-rays, electron microscopy and Raman spectroscopy. The investigated salts were mainly of olivine-like and NASICON-like structures. The X-ray diffraction and the Raman scattering show different crystalline structures, which is probably caused by difference between cores of the crystallites (probed by X-rays) and their shells (probed by the Raman scattering). Most of the Raman spectra were identified with previously published data, however in the samples with high vanadium concentration we have observed new, not reported earlier modes at 835 cm^{-1} and 877 cm^{-1} , that we identified as oscillations related to $\text{V}_2\text{O}_7^{4-}$ or VO_4^{3-} anions.

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1. Introduction

Lithium salts show very interesting phenomenon of ionic conductance when electric charge is carried by Li^+ ions moving in the crystal lattice. This effect is used for energy storage applications such as laptops, electric cars and photovoltaic power stations. Nowadays a new class of materials are being developed as active cathode materials: compounds of phospho-olivine and phospho-NASICON structures [1]. In this paper we present the Raman investigations of lithium salts: LiFePO_4 and $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ obtained by solution method [2]. These materials have low cost, good thermal stability, high theoretical capacities: 170 mAh/g and 197 mAh/g, and high open circuit voltages 3.5 V and 4.1 V, which makes them good candidates to replace presently used cobalt oxide electrodes [1–3].

2. Experimental

The analyzed samples were LiFePO_4 and $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ and their solid solutions. The LiFePO_4 -based samples were $\text{LiFe}_{1-x}\text{V}_x\text{PO}_4$ with vanadium content x_V from 0.01 up to 0.2. The $\text{Li}_3\text{V}_{2(1-x)}\text{Fe}_{3x}(\text{PO}_4)_3$ samples had iron content $x_{\text{Fe}} = 0.01, 0.03, 0.05, 0.07, \text{ and } 0.09$. All materials were obtained by solution method [2]. The composition was controlled by the inductively coupled plasma optical emission spectrometry (ICP-OES).

X-ray diffraction (XRD) characterization was conducted in Siemens D5000 or X'Pert Pro Panalytical with $\text{Cu } K_\alpha$ source in the range $2\theta = 10\text{--}80^\circ$ with 0.03° step. Scanning transmittance electron microscopy (STEM) gave an information about size and morphology of the crystals.

Micro-Raman measurements were made using a Nd:YAG laser with wavelength 532 nm. The spectral resolution was 3 cm^{-1} . Since the laser penetrates much less than one μm into the material, the near-surface region of microcrystals was analyzed.

3. Results and discussion

The XRD results (Fig. 1) indicated that undoped LiFePO_4 was in single phase olivine structure and $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ was in monoclinic NASICON-like structure [4]. The analysis of the XRD results showed that lattice parameter of $\text{LiFe}_{1-x}\text{V}_x\text{PO}_4$ decreased with increasing content of vanadium: $\Delta a/a = -0.018(6)x_V$, $\Delta b/b = -0.03(1)x_V$, $\Delta c/c = -0.008(6)x_V$. This suggested that addition of vanadium led to a mixed-cation phospho-olivine crystal containing only so small amounts of other phases, that they features could not be easily distinguished in the XRD.

The average crystallite size calculated using Scherrer's formula was 50–55 nm. On the other hand, the STEM images showed that material consisted of shapeless microcrystals that had sizes between 0.1 and 5 μm . Comparing these two results we conclude that the sample consisted of small, 50 nm crystallites agglomerated in bigger grains.

Such structure gives big surface to volume ratio, which is beneficial for the Li-ion cathode material [2]. STEM images showed that the microcrystals were coated by rather amorphous material and the cores of the crystals were highly crystalline (Fig. 2).

Crystal quality of the samples was good enough to observe a lot of sharp phonon lines in the Raman spectroscopy. The olivine vibrations are classified as internal (related to the modes of PO_4 tetrahedra) and external ones. The internal modes are assigned as ν_1, ν_2, ν_3

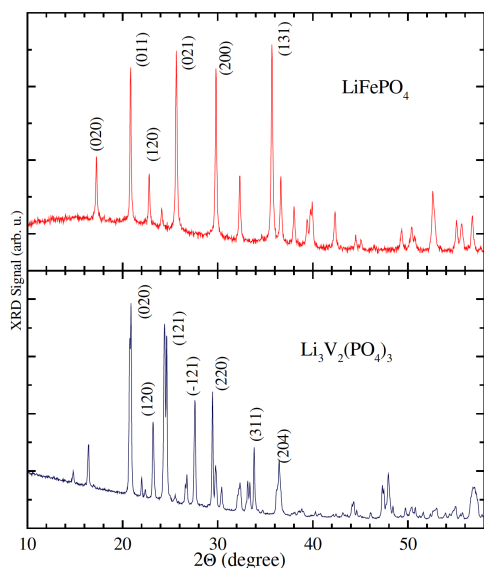


Fig. 1. XRD patterns of pure (upper) LiFePO_4 and (lower) $\text{Li}_3\text{V}_2(\text{PO}_4)_3$.

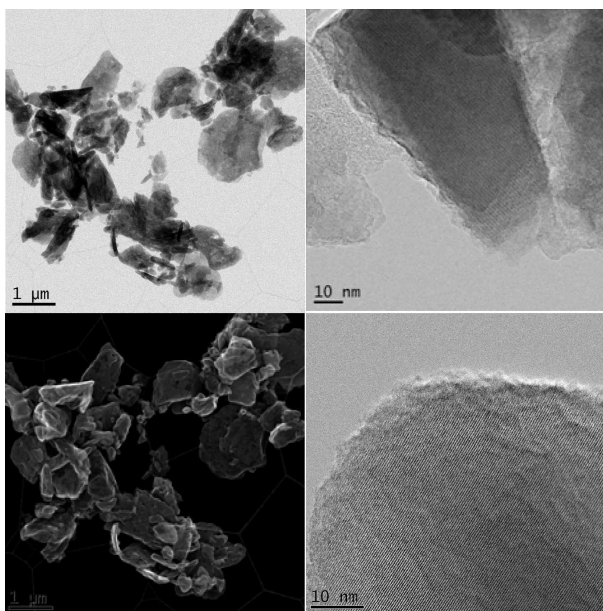


Fig. 2. Transmission electron microscope images of the samples: left — microcrystals, right — atomic structure, upper — $\text{LiFe}_{0.9}\text{V}_{0.1}\text{PO}_4$, lower — $\text{Li}_3\text{V}_2(\text{PO}_4)_3$.

and ν_4 according to Herzberg's notation for the tetrahedron modes [5].

Figure 3 shows spectra of the $\text{LiFe}_{1-x}\text{V}_x\text{PO}_4$ samples with different contents of vanadium, x_V . Most of the peaks are related to LiFePO_4 in olivine structure [6, 7]. The highest peaks at 990 cm^{-1} and 1040 cm^{-1} are most probably ν_3 modes, the 444 cm^{-1} peak is ν_2 mode. The fully symmetric $A_g\nu_1$ mode was missing in the LiFePO_4 Raman spectra. The Raman peaks were relatively broad, their widths were about 50 cm^{-1} . Both these observa-

tions suggest some distortion of the structure observed by the Raman spectroscopy. The laser light used for the Raman spectroscopy penetrates much less than $1\text{ }\mu\text{m}$ into the material, so it probes mainly the shell of the microcrystals. Comparing the Raman and the XRD results one could conclude that the crystalline quality of the core was better than the shell quality.

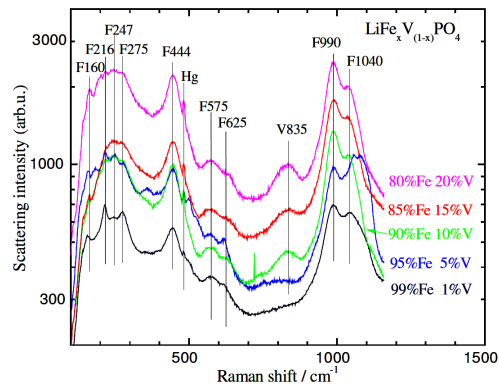


Fig. 3. Raman spectra of $\text{LiFe}_{1-x}\text{V}_x\text{PO}_4$ with different x_V . Peaks F160–F1040 are related to pure LiFePO_4 . V835 peak is related to vanadium.

The position of the Raman peaks does not change with addition of V. Only one new peak at 835 cm^{-1} was observed in the samples with vanadium. Its intensity was rising with increasing V concentration. It suggested that instead of mixed-cation compound where V replaces Fe, a new phase containing vanadium was created. These observations contradicted the XRD results. The discrepancy was due to the difference between shell and core part of the crystallites.

The Raman spectra of the $\text{Li}_3\text{V}_{2(1-x)}\text{Fe}_{3x}(\text{PO}_4)_3$ samples with different contents of iron (see Fig. 4) consisted of a lot of sharp peaks. Most of these peaks were present in the sample that had no iron. In Fig. 4 they were labelled from V144 to V1022. Only one peak at 947 cm^{-1} was correlated with iron content. It has exactly the position of expected $A_g\nu_1$ line of LiFePO_4 [7].

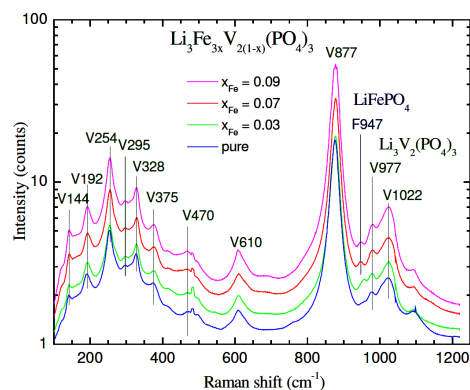


Fig. 4. Raman spectra of $\text{Li}_3\text{V}_{2(1-x)}\text{Fe}_{3x}(\text{PO}_4)_3$ with different contents of iron.

In the case of the high-vanadium samples, the Raman peaks were sharper than for the samples with a high iron content. Their widths were about 25 cm^{-1} .

The peaks at 977 cm^{-1} and 1022 cm^{-1} can be identified as related to $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ at NASICON-type structure [3, 4, 8]. However, the majority of peaks observed in these samples were not reported previously neither for iron nor for vanadium compounds. The most intense, characteristic peak, present at 877 cm^{-1} , neither was reported.

In order to establish origin of the new peaks, one should estimate frequency ν of oscillator having effective mass μ and effective force constant κ that can be calculated from classical equation

$$\nu = \frac{1}{\lambda} = \frac{1}{2\pi} \frac{1}{c} \sqrt{\frac{\kappa}{\mu}}. \quad (1)$$

For example, frequency of oxygen oscillation in P–O bond is about 1000 cm^{-1} , which is observed in many phosphates. The V–O bond is weaker than the P–O bond, its strength is $\kappa = 6.64 \text{ N/cm}$ [9], which gives oxygen oscillation frequency of about 820 cm^{-1} . So, most probably the 877 cm^{-1} peak represents oscillations of oxygen bound to vanadium. In fact, PO_4^{3-} and VO_4^{3-} anions give similar four Raman-active internal modes. The strongest lines correspond to $\nu_1(A_1)$ symmetric stretching vibration [5, 10, 11]. Comparing with orthophosphate, orthovanadate lines are shifted to the lower frequencies due to longer V–O bond length of about 1.7 \AA [12] (P–O bond length is *ca.* 1.55 \AA [13]) and resulting lower force constant κ . It was observed that the strongest peaks of LiCdVO_4 Raman spectra were at 845 cm^{-1} and 875 cm^{-1} [11]. The ν_1 mode of YVO_4 was reported at 870 cm^{-1} [14]. However, similar frequency 874 cm^{-1} was reported also for $\text{V}_2\text{O}_7^{4-}$ anion (VO_3 terminal group) [10]. So the 877 cm^{-1} line could be identified as oscillations related to VO_4^{3-} or $\text{V}_2\text{O}_7^{4-}$ anions.

The Raman investigations of LiFePO_4 and high-vanadium phosphate mixtures with ratio 1:1 showed that the vanadium-related peaks were much stronger than the peaks related to the LiFePO_4 . It was probably due to strong polarization of the V–O bonds. This observation explains why the 877 cm^{-1} peak was more than 2 orders of magnitude stronger than $\nu_1(\text{LiFePO}_4)$ peak even in samples with 9% of iron.

4. Conclusions

In the series of samples of lithium salts we have observed phonon modes related to many crystal structures, mainly olivine-like and NASICON-like.

Most of the spectra were identified with previously published data, however in the samples with high vana-

dium concentration we have observed new, not reported earlier modes (with the strongest at 877 cm^{-1}), that we identified as oscillations related to VO_4^{3-} or $\text{V}_2\text{O}_7^{4-}$ anions.

X-ray diffraction and the Raman scattering show differences in crystalline structures. The XRD data present high quality, one-phase crystals that change their lattice parameter during doping. The Raman data show new phases, not observed in the XRD. This can be explained by difference between cores of the crystallites (probed by X-rays) and shells (more polycrystalline) probed by the Raman scattering.

Acknowledgments

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