



Phase Diagram of Li_xFePO_4

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The phase diagram for Li_xFePO_4 has been determined for different lithium concentrations and temperatures. The two low-temperature phases, heterosite and triphylite, have previously been shown to transform to a disordered solid solution at elevated temperatures. This disordered phase allows for a continuous transition between the heterosite and triphylite phases and is stable at relatively low temperatures. At intermediate temperatures the proposed phase diagram resembles a eutectoid system, with eutectoid point at around $x = 0.6$ and 200°C . Kinetics of mixing and unmixing transformations are reported, including the hysteresis between heating and cooling. The enthalpy of this transition is at least 700 J/mol .
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Manuscript submitted August 29, 2005; revised manuscript received November 7, 2005. Available electronically January 18, 2006.

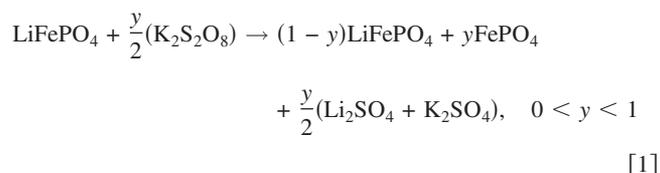
A leading candidate for positive active materials of lithium ion batteries is LiFePO_4 . Its main advantages are that it is a nontoxic, highly stable, inexpensive material, which still maintains a relatively high capacity of 170 mAh/g and a high discharge voltage of 3.5 V vs Li . One major concern about the performance of this cathode material is its low intrinsic electrical conductivity.^{1,2} Much work has been done to improve the electrical performance of LiFePO_4 by particle-size minimization,³ addition of carbon coating,^{4,5} or by doping the material with supervalent cations.⁶ When cycling at room temperature, the two phases are a lithiated triphylite phase, LiFePO_4 , and a delithiated heterosite phase, FePO_4 . Both phases are olivine-type orthorhombic structures, with the differences being the presence of lithium chains in the triphylite structure, which cause changes in the lattice parameters.

The recent discovery of a single-phase Li_xFePO_4 solid solution at temperatures of around 350°C ⁷ has spurred great interest in determining its role in the performance of LiFePO_4 as a cathode material for lithium ion batteries. We refer to this Li_xFePO_4 solid solution as disordered, since it forms at high temperatures, where entropy plays a larger role in phase stability. This seems consistent with a random mixture of lithium throughout the FePO_4 structure. We have studied the transformation of the two-phase mixture, $x\text{LiFePO}_4$ plus $(1-x)\text{FePO}_4$, to the single-phase Li_xFePO_4 for several compositions x . The unmixing transition is slow, but it is reversible with some hysteresis. The thermodynamics and kinetics of mixing and unmixing of $x\text{LiFePO}_4$ plus $(1-x)\text{FePO}_4$ ($0 \leq x \leq 1$) to form a disordered solid solution Li_xFePO_4 were the subject of the present study. Our results are summarized as a phase diagram of Li_xFePO_4 , showing temperatures where the mixing-unmixing transition occurs at different lithium concentrations. There is uncertainty in the precise phase boundaries due to sluggish kinetics. Nevertheless, the phase diagram has an overall shape expected of an unmixing system, where a continuous transformation between the low-temperature phases of heterosite and triphylite is possible by moving through a disordered phase at higher temperatures. For the composition of $x = 0.6$, however, the disordered solid solution is stable at relatively low temperatures, much as for a eutectoid transformation.

Experimental

Chemical delithiation.— LiFePO_4 material was prepared by a solid-state reaction consisting of a mixture of iron(II) oxalate $\text{Fe}(\text{C}_2\text{O}_4) \cdot 2\text{H}_2\text{O}$, ammonium dihydrogen phosphate $\text{NH}_4\text{H}_2\text{PO}_4$, and lithium carbonate Li_2CO_3 in the molar ratio (1:1:0.5). The precursors were mixed by ball milling in acetone overnight. The resulting gel was dried at 60°C under vacuum, thoroughly reground, and

heated under purified N_2 gas for 24 h at 700°C .⁸ We delithiated this material chemically by use of potassium persulfate ($\text{K}_2\text{S}_2\text{O}_8$) in an aqueous solution, as follows



The $\text{K}_2\text{S}_2\text{O}_8/\text{K}_2\text{SO}_4$ redox couple has a Nernst standard potential of approximately 5 V vs Li/Li^+ , which is higher than the 3.5 V vs Li/Li^+ for $\text{Li}_{0.0}\text{FePO}_4/\text{Li}_{1.0}\text{FePO}_4$ couple. Therefore, $\text{K}_2\text{S}_2\text{O}_8$ can oxidize LiFePO_4 to full delithiation. An aqueous solution of $\text{K}_2\text{S}_2\text{O}_8$ and LiFePO_4 was mixed at ambient temperature for 24 h, allowing equilibrium to be reached. By altering the molar ratio of $\text{K}_2\text{S}_2\text{O}_8/\text{LiFePO}_4$, samples with different amounts of lithium were prepared.

Heat-treatment.— The samples were purged with argon and vacuum-sealed in borosilicate glass ampules, then heated in a tube furnace. After heat-treatments, the samples were taken out of the furnace and cooled quickly by blowing pressurized air over them. Water quenching was also tested, giving similar results. The samples were then removed from the glass, and measured by X-ray diffraction (XRD). By using the glass tubes for heating, we were able to monitor the sample reaction over long times, which we could not do with a high temperature XRD stage.

X-ray diffraction.— An X-ray diffractometer with $\text{Cu K}\alpha$ radiation (PANalytical X'Pert PRO X'Celerator) was used to analyze and identify the phases in the material. Samples were mixed with a silicon standard powder to ensure accuracy in peak position determinations. Rietveld analysis was used to determine phase fractions present by using Philips X'pert Plus software (PANalytical). At low temperatures the system is a two-phase mixture, with nearly all the lithium in the triphylite phase. The fraction of triphylite (LiFePO_4) in the sample before heat-treatment was determined by Rietveld analysis, and was used as a measure of the concentration of lithium in the sample. After heat-treatment, samples were again analyzed with Rietveld analysis.

Differential scanning calorimetry (DSC).— Two different Netzsch differential scanning calorimeters (DSC 404C and STA 449C) were used to scan samples at a $5^\circ\text{C}/\text{min}$ rate from room temperature to 400°C and then back down to room temperature. The heat measurement of the Netzsch DSC 404C showed more distinct peaks, representative of mixing and unmixing in the sample, and therefore results using this instrument are reported. The sample was purged with argon throughout the measurements.

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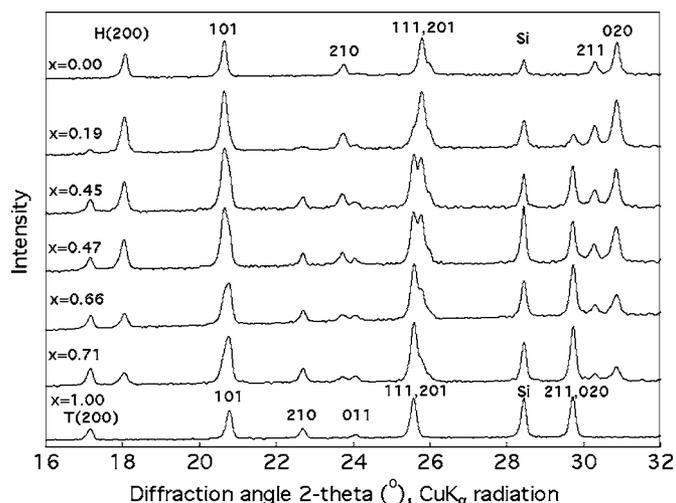


Figure 1. XRD patterns for samples with various delithiation. The amount of lithium in the sample is indicated as x . Diffraction peaks are labeled for the $Pnma$ orthorhombic structure of heterosite (H) and triphylite (T).

Results

Several samples prepared by chemical delithiation were studied in detail. The states of lithiation of the Li_xFePO_4 samples were $x = 0.19, 0.45, 0.47, 0.66,$ and 0.71 . Figure 1 shows the XRD patterns for these samples. Diffraction patterns for $x = 0$ and $x = 1$ (heterosite and triphylite) are also shown, and indexed for the orthorhombic $Pnma$ structures.

Samples with $x = 0.00$ and 1.00 were stable up to 400°C , as reported previously.⁹ However, samples with intermediate lithium concentrations showed structural changes upon heating to above 200°C . Some results were obtained by use of a high-temperature stage on the X-ray diffractometer, but since the kinetics of the transformation were sluggish at temperatures below 300°C , heat-treatments for phase fraction determinations were performed for long times on samples in glass ampules, followed by quenching. After air-quenching the samples, the phase structure was quite stable, with little change back toward the original phases, even after a week at room temperature.

A kinetics study was made at three temperatures, 220, 260, and 380°C , using the delithiated sample with $x = 0.47$. Heat-treatment times varied from 30 min to 4 days. At 380°C , the sample reached equilibrium quickly, with transformation to a disordered solid solution being complete even after 30 min. For lower temperatures of 260 and 220°C , equilibration takes a longer time, with measurements taken after 12 h of heating differing from those taken after 2 h. Between 12 h and 3–4 days the changes were smaller, however. The percentages of the disordered phase present in each sample as a function of time, determined by Rietveld refinement, are shown in Fig. 2 for the three temperatures.

A 12 h isothermal hold of the samples was selected for a further assessment of the equilibrium state. Although the samples did not reach equilibrium within 12 h, especially at temperatures below 300°C , the formation or loss of phases at different temperatures for a specific composition identified the equilibrium tendencies of the system. Figure 3 shows a series of X-ray scans for samples of $x = 0.47, 0.66,$ and 0.71 heated to different temperatures for 12 h. It is easy to see the extent of formation of the disordered solid solution from the initial mixture of the heterosite and triphylite phases by looking at the angles between 16 and 19° (200 peaks) and also at 29 to 31° (020 and 211 peaks). The transformation begins at 200°C , and the solid solution is distinct at 220°C , where all three phases are present. At 260°C , each sample consists of two phases, the disor-

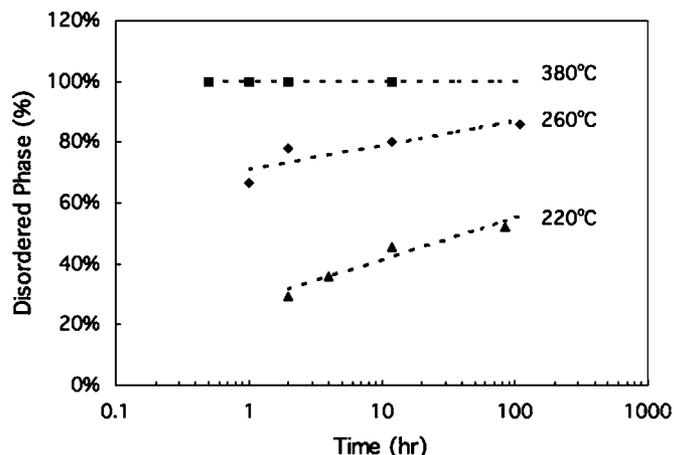


Figure 2. Comparison of kinetics of formation of disordered phase from samples with lithium composition $x = 0.47$. The percentage of disordered phase in each sample is plotted as a function of time held at the following temperatures: 220°C (\blacktriangle), 260°C (\blacklozenge) and 380°C (\blacksquare).

dered phase and either triphylite (for $x = 0.71, 0.66$) or heterosite (for $x = 0.47$). The complete transition to the disordered solid solution is found for samples treated to above 300°C .

The reversibility of the transformation to the disordered solid solution from heterosite and triphylite was confirmed in the course of formulating a phase diagram. The unmixing of the disordered solid solution is sluggish at room temperature, perhaps even imperceptible, but at higher temperatures the kinetics for unmixing are faster. Figure 4 shows a series of $x = 0.45$ samples that were heated to 380°C for 2 h to form the disordered solid solution, and then held at lower temperatures for unmixing. For temperatures of 220°C and above, no unmixing is evident. However, some separation of 200, 020, and 211 diffraction peaks can be seen at $200, 180,$ and 160°C . At these temperatures, complete unmixing does not occur within 12 h.

To further understand the thermodynamics of this system, we performed DSC measurements with the $x = 0.47$ sample to determine enthalpies of mixing and unmixing. A DSC scan is shown in Fig. 5 for both heating and cooling. For a scanning rate of $5^\circ\text{C}/\text{min}$, the enthalpy of mixing was found to be 500 J/mol , with a peak temperature of 224°C . Upon cooling, the enthalpy of unmixing was found to be 700 J/mol , with a peak at 136°C . The lower enthalpy upon heating could be a result of gradual mixing over a wide temperature range. The data is consistent with the XRD results that show the formation of the disordered solid solution beginning at approximately 200°C and continuing up to 300°C . After the DSC measurement, the sample was analyzed again with XRD, showing a structure with 200 peaks separated, but not to the original triphylite and heterosite peak positions. (The sample had not decomposed to the original two phases.) If allowed longer times, the enthalpy of unmixing is expected to be higher than our reported values. Unfortunately, slower scans gave signals that were too weak to quantify.

Discussion

The transformation of the two phases, heterosite and triphylite, to a disordered solid solution has been shown, along with the reverse transformation. Many characteristics are similar to those reported by Delacourt et al.,⁷ but since our heat-treatments were for longer times, with samples approaching equilibrium, we found some differences. The formation of the disordered solid solution occurs at temperatures of around 200°C . At 220°C , the samples with lithium concentrations of $x = 0.45, 0.47, 0.66,$ and 0.71 all showed a mix of all three phases (heterosite, triphylite, and disordered) after 12 h of equilibration. For the $x = 0.45$ and 0.47 samples, the triphylite phase disappeared above 220°C , leaving only a mix of heterosite and the

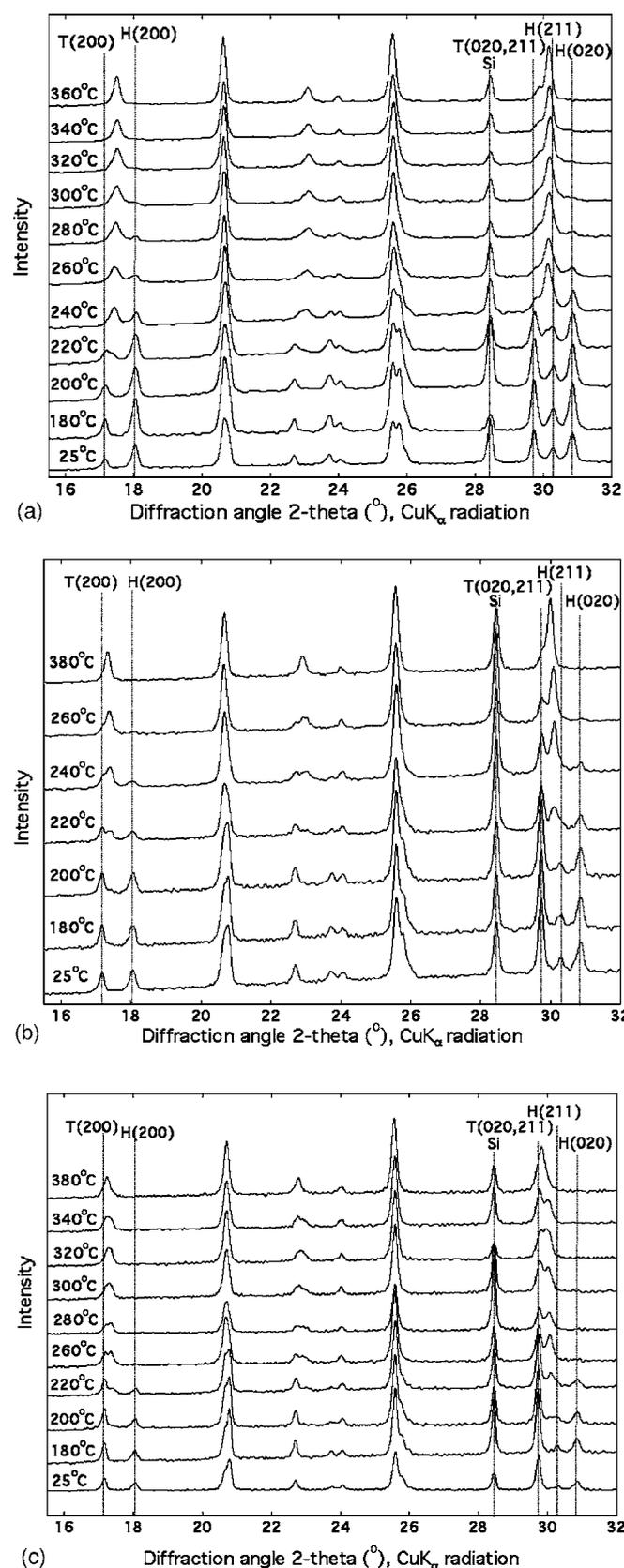


Figure 3. Series of XRD patterns for samples with lithium composition: (a) $x = 0.47$, (b) $x = 0.66$, and (c) $x = 0.71$. Each sample was held at the noted temperature for 12 h, and then quenched to room temperature.

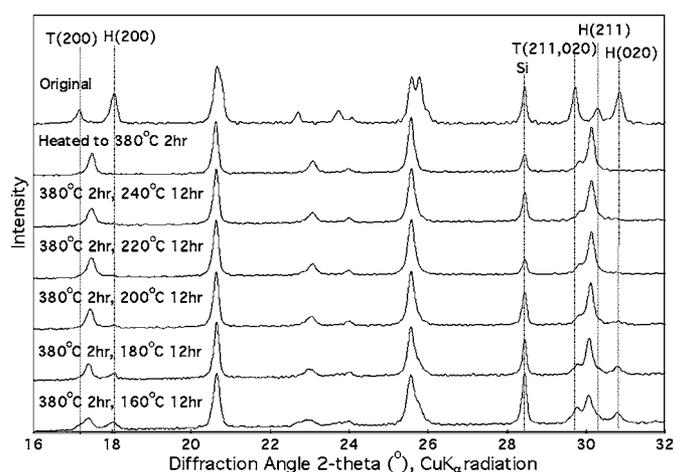


Figure 4. Comparison of XRD structure of $x = 0.45$ sample to sample heated to 380°C for 2 h, and to samples similarly heated and then cooled at the indicated temperatures. The cooling time was 12 h. The separation of the samples into distinct phases is evident, especially upon cooling to 180 and 160°C.

disordered solid solution. For the $x = 0.71$ sample, the opposite occurred, with a disappearance of the heterosite phase. For the $x = 0.19$ sample, the XRD peak positions of the disordered solid solution varied with temperature, and the transformation was not complete until heating at 300°C.

After formation of the disordered solid solution at high temperatures, unmixing occurs at temperatures below 200°C. During unmixing, the heterosite and triphylite phases reform, with slightly shifted lattice parameters. These reformed phases indicate the equilibrium structures at each temperature. Assuming the orthorhombic lattice constants follow Vegard's law as suggested by Ref. 7 and by the present results, the equilibrium compositions in the unmixed state were calculated for temperatures between 160 and 220°C.

Our best estimate of the phase diagram is shown in Fig. 6. We propose that the phase diagram is an unmixing diagram with some characteristics of a eutectoid transformation. Rietveld refinement was used to determine phase fractions at each temperature. Our

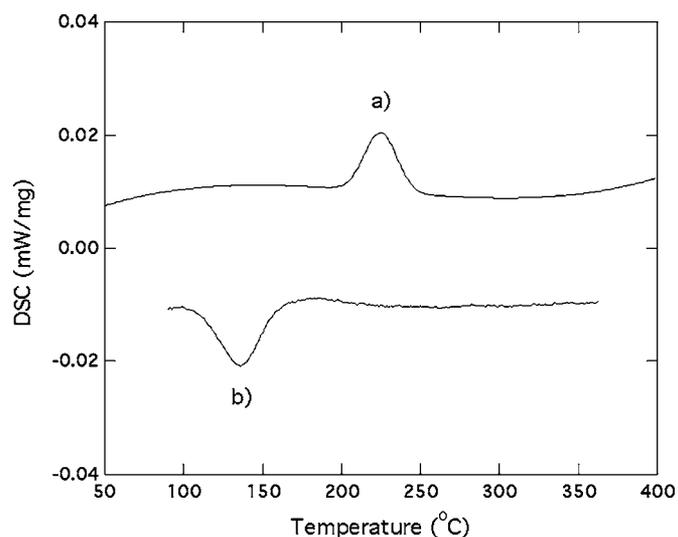


Figure 5. DSC scan of $\text{Li}_{0.47}\text{FePO}_4$ sample from room temperature to 400°C. During heating, the endothermic peak (a) has a measured enthalpy of 500 J/mol. The exothermic peak (b) formed during cooling was measured as 700 J/mol.

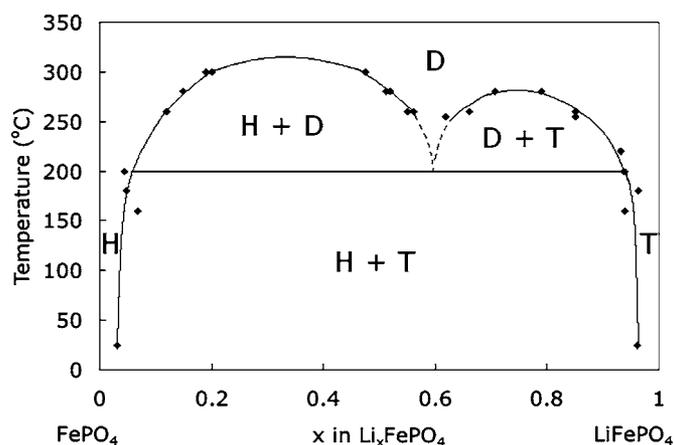


Figure 6. Phase diagram of LiFePO_4 (T, for triphylite) and FePO_4 (H, for heterosite) phases showing their merging to a solid solution (D, for disordered) in a eutectoid system. Data points at 25°C are based on published work by Yamada et al.¹⁰ The eutectoid point is around the composition $x = 0.6$ and temperature 200°C. Above 200°C, mixtures of heterosite or triphylite and the disordered phase were seen up to around 300°C. Above 300°C, the disordered phase dominates.

samples consisted of two phases at temperatures between 260 and 300°C, so we were able to use the measured phase fractions and the lever rule to determine several points on the phase diagram. Additional points at 220°C and below were calculated based on the lattice parameters of reformation of heterosite and triphylite upon cooling the disordered solid solution. The points indicate that the eutectoid point occurs around composition $x = 0.6$ and temperature 200°C. For temperatures below 260°C, equilibrium takes a much longer time, so it is difficult to pinpoint the phase boundary for the disordered phase near the composition $\text{Li}_{0.6}\text{FePO}_4$. However, after several weeks at 240°C, a $\text{Li}_{0.6}\text{FePO}_4$ sample was completely disordered. Generally, samples of $\text{Li}_{0.6}\text{FePO}_4$ composition required less time and lower temperatures to disorder compared to other compositions.

The presence of narrow monophasic regions near the stoichiometric end members of LiFePO_4 and FePO_4 at room temperature has been suggested recently by Yamada et al.¹⁰ The range of these monophasic regions are from $x = 0.00$ to 0.03 and $x = 0.96$ to 1.00 . Their results were added as data points to our phase diagram at room temperature, since compositions $x = 0.03$ and 0.96 mark a transition between a monophasic region equivalent to a disordered solid-solution phase and the two-phase mixture of heterosite plus triphylite.

Figure 7 shows the 2-theta positions of the 200 diffractions for the $x = 0.45$ sample, plotted against heat-treatment temperature. The plots include two sets of data, one shows the peak positions for the delithiated sample heated to each temperature, the second shows the peak positions after cooling for 12 h after first heating to the disordered state. The formation of the peak from the disordered solid solution occurs when the heterosite and triphylite peaks are still retained, indicating a nucleation-and-growth-type of phase transformation. For both heating and cooling, there is a hysteresis of about 80°C between the temperatures where the 200 peaks from the disordered solid solution first appears, and the temperature where the transformation is complete. The unmixing from the disordered solid solution does not happen readily within 12 h. However, it is evident that upon cooling, the samples unmix to form the original heterosite and triphylite compositions, in addition to the disordered solid solution.

Ordinarily, one expects two compositional ranges for disordered solid solutions in unmixing systems, and this is the case for the present phase diagram at temperatures below 200°C. Conventional unmixing phase diagrams are readily understood from free energy vs

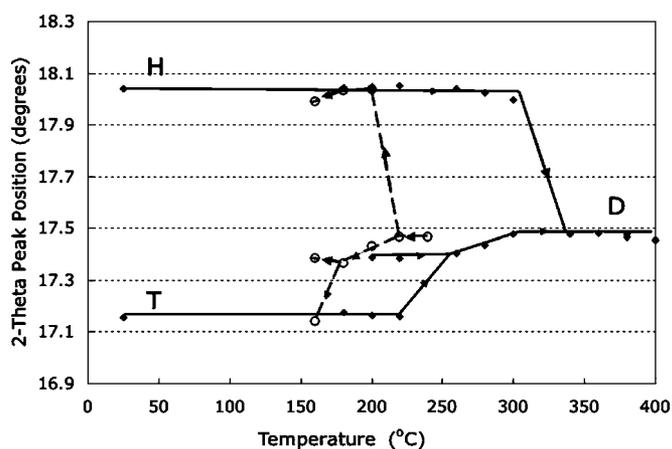


Figure 7. Positions of 200 peaks as a function of temperature. Data are shown for a sample with $x = 0.45$. The solid symbols (\blacklozenge , connected by solid lines) are peak positions from samples heated to the specified temperatures for 12 h. The open symbols (\circ , connected by dashed lines) are from samples first heated to 380°C for 2 h, and then held at the specified temperatures for 12 h.

composition curves when interatomic interactions between unlike pairs of atoms are unfavorable. In the present system, the unmixing tendency is between Li ions and vacant sites, which have a repulsive effective interaction. At intermediate temperatures from 200–300°C, however, the phase diagram of Fig. 6 shows three composition ranges for disordered solid solutions. The phase diagram of Fig. 6 implies two zones where the free energy of mixing is unfavorable, unlike the usual case of one maximum near the middle of the composition range. This is a characteristic of eutectoid transformations, where the three phases are distinct. For the case of Li_xFePO_4 , it is less obvious what distinguishes the phase with composition near $x = 0.6$. We have found no evidence for chemical ordering, although X-ray diffractometry is not highly sensitive to the spatial order of Li atoms. Changes in Li concentration do cause large changes in lattice parameter and alter the shape of the unit cell in Li_xFePO_4 . Such differences would alter the enthalpy or entropy for unmixing, but it is not obvious how this would provide a local minimum in free energy near $x = 0.6$.

Conclusion

The mixing transformation from the heterosite and triphylite phases to a disordered solid solution of Li_xFePO_4 occurs around 200°C. Between 200 and 300°C, a mixture of disordered solid solution and either heterosite or triphylite is present. Above 300°C, all Li_xFePO_4 samples equilibrated to form a disordered solid solution. The phase diagram for this system indicates that there are three compositional ranges where the disordered solid solution is stabilized at intermediate temperatures, near $x = 0.0$, 0.6 and 1.0 . The heat of transformation was measured for an $x = 0.5$ sample, and is estimated to be at least 700 J/mol.

Acknowledgments

The authors thank Dr. Khalil Amine, Dr. Ilias Belharouak, and Argonne National Laboratory for providing the LiFePO_4 material. This work was supported by the U.S. Department of Energy under grant DE-FG03-00ER15035.

California Institute Of Technology assisted in meeting the publication costs of this article.

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