

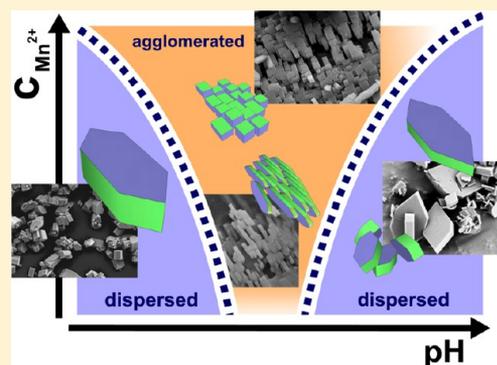
# Morphology and Agglomeration Control of LiMnPO<sub>4</sub> Micro- and Nanocrystals

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## Supporting Information

**ABSTRACT:** Microwave-assisted hydrothermal synthesis was used to grow LiMnPO<sub>4</sub> micro- and nanocrystals from acetate precursors. By appropriate adjustment of the precursor concentration and the pH-value of the reactant, the product composition and purity along with the crystal size can be manipulated, resulting in particle-dimensions from around 10 μm down to a few 100 nm. Prisms and plates with hexagonal basal faces as well as cuboid and rod-like particles were produced. The effects on the crystal morphology as well as on the materials texture and agglomeration tendency are discussed and a comprehensive agglomeration phase diagram is constructed.



## INTRODUCTION

The properties of crystalline nanomaterials are intimately connected with their size, shape, and microstructure so that downsizing and tailoring the morphology of materials provides control about, e.g., their electronic, magnetic, and optical properties.<sup>1,2</sup> In addition to the properties of primary particles, their tendency to form aggregates is highly relevant for tailoring desired materials optimized regarding the basic physicochemical parameters as well as, e.g., their overall toxicity, reactivity, and mechanical stability. Therefore, understanding and controlling accretion of nanocrystals and their oriented or random agglomeration to larger, possibly textured entities is a precondition for adjusting a particular property for the desired application.<sup>3</sup> In addition, research activities do not only focus on improving materials for particular applications but include the issue of cost and energy efficient production routes for environmentally benign materials.<sup>4,5</sup>

A particularly relevant application of nanostructured materials is their usage as electrode materials in electrochemical energy storage devices, where, e.g., Li-diffusion, electronic conductivity, and structural stability have to be optimized (see e.g., refs 6–8). In particular, reduction of the ionic and the electronic diffusion lengths and increase of the surface to volume ratio often yields significant improvements in the electrochemical activity. This is particularly illustrated by the olivine phosphates LiMPO<sub>4</sub> with M = (Mn, Fe, Co, Ni)<sup>9–12</sup> which can be applied in lithium-ion batteries nanosized only. Olivine LiMnPO<sub>4</sub> is a promising cathode material, owing to the Mn<sup>2+</sup>/Mn<sup>3+</sup> redox potential at 4.1 V vs Li and the associated flat discharge curve.<sup>14</sup> Stable reversible capacities of up to 145 mAh/g have already been obtained in carbon-coated nanostructured material consisting of ~30 nm thick platelets which extend several 100 nm in the base plane<sup>15</sup> while the

performance of rather spherical particles decreases significantly for particle sizes exceeding ~200 nm.<sup>16</sup> In addition to the bare size reduction of the particles, the particular morphology is relevant as well, since the ionic diffusivity was predicted to be not only small but also strongly anisotropic in bulk materials, favoring the crystallographic *b*-direction.<sup>13</sup> Experimental evidence for this anisotropy is indeed deduced from recent studies on nanostructured materials<sup>15,17</sup> and from single crystals.<sup>18</sup> These results imply that nonspherical crystals with shortest dimensions along the crystallographic direction(s) of high ionic conductivity are optimal for actual applications in lithium-ion batteries. Furthermore, the orientation and the contact of the particles with respect to each other, to the electrolyte, and to the current collector have notable influence on the electrochemical performance of a material.<sup>19</sup> Therefore, the particles' surface properties must be adjusted not only to meet the demands of conductivity and chemical stability, but also of the particle distribution and agglomeration, which are governed by surface charging effects. In addition to their applicability for energy storage, the olivine phosphates exhibit antiferromagnetic spin order and a large magnetoelectric effect in the magnetically ordered phase, which is of fundamental research interest but may also yield future applications as well.<sup>20</sup> This is highlighted by the recent discovery of unusual ferrotoroidic domains in LiMPO<sub>4</sub> with M = Co or Ni, which is discussed in terms of future data storage devices.<sup>21</sup>

In this work, we investigate the tailored synthesis of dispersed and agglomerated LiMnPO<sub>4</sub> with dimensions between ~100 nm and several μm aiming at fundamental

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information which enables tailoring nano- and microscaled material. We demonstrate that control of the size and shape of  $\text{LiMnPO}_4$  crystals as well as of the particles' tendency toward (oriented) agglomeration is possible by applying a fast and low-energy synthesis route, starting from environmentally harmless and nonhazardous precursors. The microwave-assisted hydrothermal method applied here allows controlled synthesis at relatively low temperatures with a nontoxic solvent. Because of their good solubility in water and absence of any additional environmental impact, acetates were selectively chosen as cation-precursors. The phosphate source (diammonium hydrogen phosphate) is commonly used as fertilizer in agriculture. Besides ammonia, no further organic additives were used in the educt, thus rendering the chosen synthesis route elementary and reproducible.

## ■ EXPERIMENTAL SECTION

Applying a hydrothermal synthesis technique,  $\text{LiMnPO}_4$  was synthesized using lithium acetate dihydrate, manganese(II) acetate tetrahydrate, and diammonium hydrogen phosphate (Aldrich,  $\geq 99\%$ ) solved in deionized water in an off-stoichiometric ratio of 3:1:1 with respect to the ratio of the Li-, Mn-, and  $\text{PO}_4$ -ions. The concentration of the Mn-ions in the solution was adjusted to a value between 0.03 and 0.13 mol/L. The pH-value of the reactant was measured with a SevenGo SG2 system (Mettler Toledo) and, starting from a value of 5.5–5.8, adjusted to a value of up to 11.5 by adding diluted ammonia (AppliChem).

Ten milliliters of the solution was put into a 30 mL glass reaction vessel equipped with a magnetic stir bar, which was transferred into a Monowave 300 microwave reactor (Anton-Paar) with 2.46 GHz radiation.<sup>22</sup> Within a ramping time of 10 min, the vessel was heated to a fixed temperature between 160 and 220 °C and held at this temperature for 20 min. Subsequent cooling was carried out by the use of compressed air. Note that high precursor concentrations and superalkaline pH-values could not be achieved simultaneously due to pressure limitations of the device since the vapor pressure of the ammonium adds to that of the other educts. After the synthesis procedure, the precipitate was recovered from the vessel, washed several times with deionized water and ethanol, and dried at 90 °C overnight.

The energy efficiency of the applied microwave system can be roughly estimated by considering the radiation power for one of the synthesis procedures. The total energy deposit upon heating up the reaction chamber and the educts amounts to about 28 kJ. However, heating 10 mL of water and the glass reaction vessel (54 g) from 20 to 220 °C consumes ~8.4 kJ (+0.3 kJ vaporization heat) and ~7.6 kJ, respectively. Neglecting any effects due to the chemical reaction hence implies that the efficiency of this laboratory system is roughly about 50%. Note, that this value may be easily increased when up-scaling and optimizing the process so that the method offers very high efficiency compared to any ceramic or conventional hydrothermal procedures.

X-ray powder diffraction (XRD) was performed in Bragg–Brentano geometry (Siemens D500) applying  $\text{Cu-K}_{\alpha 1}$  and  $\text{Cu-K}_{\alpha 2}$  radiation ( $\lambda_{1/2} = 1.54056/1.54433$  Å). The measurements were taken in the  $2\theta$  range from 10° to 70° with a step size of 0.02° and integration time of 1 s (short) or 10 s (long) per step. Prior to the measurements, the powders were dispersed in isopropyl alcohol and dripped on a glass sample carrier. Structural phase analysis was conducted with the FullProf Suite 2.0 program.<sup>23</sup> The morphology of the material was studied by means of a ZEISS Leo 1530 scanning electron microscope with an acceleration voltage of 9 kV. Preliminarily, the samples were coated with a thin gold layer of about 10 nm with a Balzers Union SCD 004 sputtering device under Argon atmosphere.

## ■ RESULTS AND DISCUSSION

**Synthesis Parameters.** Solutions of the individual precursors are pellucid and show a pH-value of 8.1

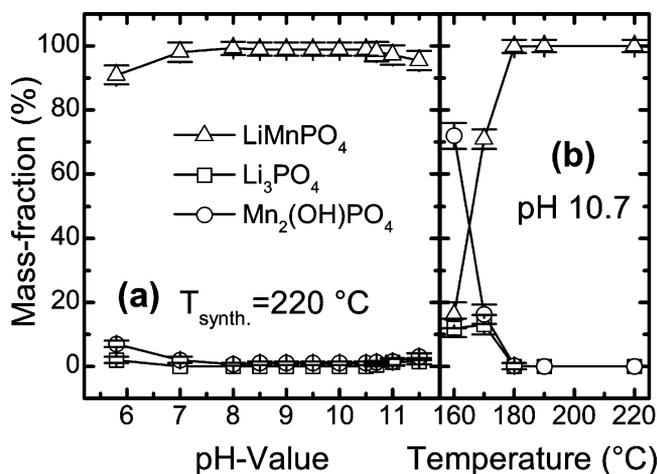
( $(\text{CH}_3\text{COO})\text{Li}$ ), 7.5 ( $(\text{CH}_3\text{COO})_2\text{Mn}$ ) and 8.1 ( $(\text{NH}_4)_2\text{HPO}_4$ ), which is a result of the soft basic properties of  $\text{CH}_3\text{COO}^-$  and  $\text{HPO}_4^{2-}$  ions. A white precipitate is formed upon mixing of dissolved  $(\text{NH}_4)_2\text{HPO}_4$  and  $(\text{CH}_3\text{COO})_2\text{Mn}$ , which is accompanied by a drop of pH-value to 5.5. The addition of  $(\text{CH}_3\text{COO})\text{Li}$  has little effect. No color change can be observed upon alkalizing the solution with ammonia up to a pH of around 10.7. Above this value, the color changes to beige and eventually brown, possibly because of the oxidation of  $\text{Mn}^{2+}$  to Manganite or manganese dioxide with air oxygen.

In order to investigate the white precipitate, solutions with pH of 5.5 (starting solution), 9, and 11 were dried, and the products were measured by means of XRD (see the Supporting Information, SI). All three samples exhibit the diffraction pattern typical for  $\text{NH}_4\text{MnPO}_4 \cdot \text{H}_2\text{O}$ .<sup>24</sup> However, the XRD patterns of the samples prepared at pH 5.5 and 11 show a high background, which points to the presence of amorphous phases. The sample prepared at pH 9 exhibits sharp peaks and a low background that is characteristic for good crystallinity. All samples show a high degree of particle orientation in the (010) plane, which is most pronounced in the sample prepared at pH 9. This predominant alignment can be explained by the plate-like morphology of the obtained crystallites (for electron micrographs, see the SI).

The subsequent hydrothermal syntheses as described above yield white to beige colored powders. The pH of the reaction products as recovered from the microwave reactor under-matched the pH of the solutions before reaction by an average value of 1. All washed and dried materials were studied by powder XRD and characteristic patterns of the olivine *Pnma* structure realized in  $\text{LiMnPO}_4$  were found (see the SI). A rough inspection of the data shows that several samples exhibit  $\text{Li}_3\text{PO}_4$  and  $\text{Mn}_2(\text{OH})\text{PO}_4$  phases in addition to the main phase. Hence, a continuative phase analysis was made for each sample by executing a basic multicomponent phase refinement of the XRD patterns by fitting the mass fractions of the three compounds  $\text{LiMnPO}_4$  (ICSD #97763<sup>25</sup>),  $\text{Li}_3\text{PO}_4$  (ICSD #25816<sup>26</sup>), and  $\text{Mn}_2(\text{OH})\text{PO}_4$  (ICSD #16928<sup>27</sup>) with pseudo-Voigt profile functions. The results of this analysis for materials synthesized with a fixed precursor concentration of 0.03 mol/L with respect to the  $\text{Mn}^{2+}$ -ions in the starting solution are shown in Figure 1 for various pH-values of the reactant and synthesis temperatures.

The data in Figure 1(a) show that, at the synthesis temperature of 220 °C, the production of phase-pure  $\text{LiMnPO}_4$  without formation of side products is possible in a wide pH-range between 7 and 10.7. Below and above this regime, the materials exhibit  $\text{Li}_3\text{PO}_4$  and  $\text{Mn}_2(\text{OH})\text{PO}_4$  impurity phases in the %-range, which can be detected by the XRD experiment. Note that most of the overview XRD patterns were measured with a short integration time so that the error bars are in the range of a few mass-percent. The XRD patterns discussed in the next sections were more accurately measured.

The regime of stable  $\text{LiMnPO}_4$  production coincides with the pH-range favoring crystalline  $\text{NH}_4\text{MnPO}_4 \cdot \text{H}_2\text{O}$  without amorphous side products. This compound is known to be a precipitate precursor at the synthesis of  $\text{LiMnPO}_4$  due to its structural similarities.<sup>28,29</sup> We thus assume that  $\text{NH}_4\text{MnPO}_4 \cdot \text{H}_2\text{O}$  is a necessary precursor for the synthesis of  $\text{LiMnPO}_4$  under these conditions. The residual amorphous phases present in the educt are likely to be reacted to the impurity phases  $\text{Li}_3\text{PO}_4$  and  $\text{Mn}_2(\text{OH})\text{PO}_4$ . Note that calculations in ref 30 suggest that a production of  $\text{Li}_3\text{PO}_4$  is



**Figure 1.** (a) Weight fraction of  $\text{LiMnPO}_4$ ,  $\text{Li}_3\text{PO}_4$ , and  $\text{Mn}_2(\text{OH})\text{PO}_4$  in dependence of (a) the educt pH-value at fixed temperature and (b) the synthesis temperature at fixed pH-value as deduced from Rietveld fits to the XRD data.

more likely at superalkaline conditions which favor the phosphate form  $\text{PO}_4^{3-}$  in aqueous solutions. This conclusion is supported by the results at hand.

In Figure 1(b), the effect of synthesis temperature variation is illustrated for fixed  $\text{pH} = 10.7$ . The data show that, under these conditions, phase pure synthesis of  $\text{LiMnPO}_4$  occurs at synthesis temperatures exceeding  $180\text{ }^\circ\text{C}$ . In general, the results in Figure 1 demonstrate that with the chosen precursors, the experiment offers a wide range of parameters where  $\text{LiMnPO}_4$  can be successfully synthesized while their variation may be used to control the morphology and the size of the produced particles. In the following, the synthesis temperature was chosen to be  $220\text{ }^\circ\text{C}$  in all cases.

**Particle Size and Morphology.** Figure 2 gives an exemplary overview on the  $\text{LiMnPO}_4$  morphologies accessible by the applied synthesis route. The presented electron micrographs are grouped according to the three different precursor concentrations (L:  $0.03\text{ mol/L Mn}^{2+}$ -ions; M:  $0.075\text{ mol/L Mn}^{2+}$ -ions; H:  $0.13\text{ mol/L Mn}^{2+}$ -ions) which were used. Within each group, the images are arranged with respect to the pH-value of the reactant before the synthesis.

The largest  $\text{LiMnPO}_4$  crystals are obtained at a low precursor concentration and neutral to alkaline pH-values. Sample L1 consists of hexagonal prisms with a base-length of about  $10\text{ }\mu\text{m}$  and a height of  $3\text{ to }5\text{ }\mu\text{m}$ . As demonstrated by the following images, the hexagonal basal face is a typical element of hydrothermally synthesized  $\text{LiMnPO}_4$  particles (cf. also ref.31). Increasing the pH-value to 9 (sample L2) affects both the crystal size and the agglomerative behavior of the particles. The material features rectangular aggregates with an ordered texture and consisting of sub- $\mu\text{m}$ -sized cuboidal particles. This strong tendency toward aggregation disappears when the reactant is heated at even more alkaline conditions. Sample L3 produced at  $\text{pH } 10.7$  contains arbitrarily arranged platelets, again with a hexagonal however rounded basal face. The longest edge amounts  $1\text{--}2\text{ }\mu\text{m}$  and the platelet heights are sub- $\mu\text{m}$ . The smallest particles obtained at this precursor concentration were produced at  $\text{pH}$  of 11.5, which is the highest pH-value applied. While the morphology of the resulting particles is similar to sample L1, the crystals are sub- $\mu\text{m}$  to nanosized in any direction. Note, however, that under these strong alkaline

conditions, no phase pure  $\text{LiMnPO}_4$  synthesis was possible (see Figure 1).

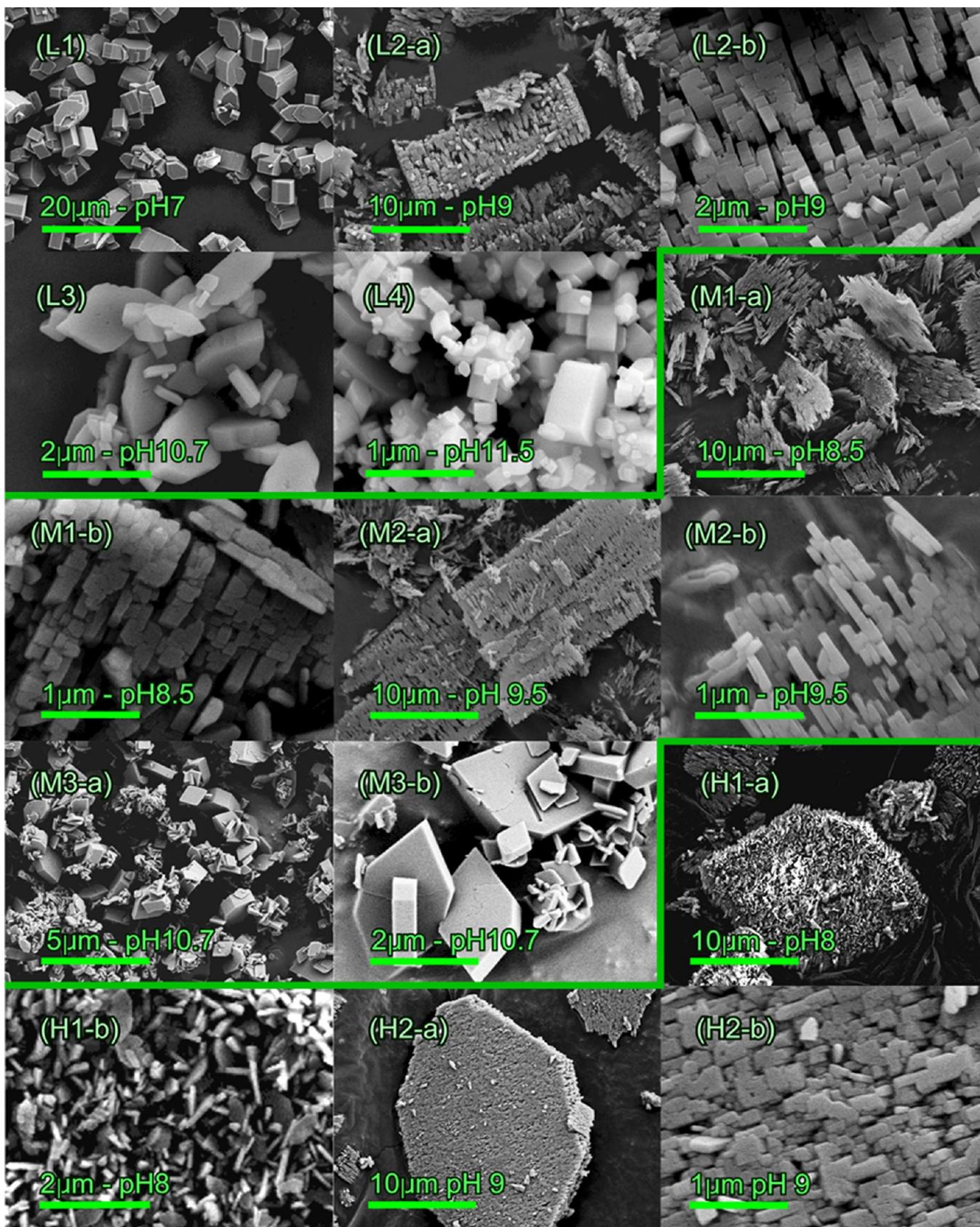
The above-described tendency toward agglomeration into ordered textures intensifies when increasing the precursor concentration. At a pH-value of 8.5 (sample M1), the process yields plates with dimensions of about  $10\text{ }\mu\text{m}$  consisting of cuboidal particles with a typical size of some  $100\text{ nm}$ . A similar hierarchically assembled structure is realized in sample M2, synthesized at  $\text{pH } 9.5$ . When increasing the pH-value, the size of the agglomerated structures extends. Concomitantly, growth of the individual particles seems to favor a particular direction, which yields rod-like crystals with a typical length of about  $0.5\text{ }\mu\text{m}$ , being the elements of the agglomerates (see images M2-a and M2-b). Further rise of alkalinity to  $\text{pH} = 10.7$  (sample M3) stops the strong aggregative tendency. Sections M3-a and M3-b of Figure 2 display well-developed hexagonal platelets, however with a very broad size distribution with in-plane particle dimensions from about  $2\text{ }\mu\text{m}$  down to some  $100\text{ nm}$ .

At the highest precursor concentration of  $0.13\text{ mol/L Mn}^{2+}$ -ions, textured agglomerates are observed in the whole accessible pH-range. All materials exhibit well-ordered agglomerates with hexagonal to octagonal shape and sizes larger than  $10\text{ }\mu\text{m}$ . The electron micrographs of sample H1, synthesized at an educt pH-value of 8, indicates that the aggregates consist of non- or low-ordered sub- $\mu\text{m}$  particles. Note, that the structure analysis described below reveals that the crystallites exhibit an ordered texture, thus rendering the apparent disorder surface related. This is more clearly visible in the micrographs H2-a and b of the material produced at  $\text{pH } 9$ . Here, the ordered texture of the agglomerates surface formed by cuboidal particles with a typical size of some  $100\text{ nm}$  is well visible. Interestingly, the flake-like aggregates can be multilayered, thereby forming “agglomerates of agglomerates”. Note that neither the morphology of the primary particles nor of the aggregates changes when the educt pH is increased 10.4 (not shown).

Summarizing, variation of the precursor concentration and the pH-value of the reactant strongly affects the size and shape of the individual crystallites and of the agglomerates. Note, that the particles morphologies obtained after hydrothermal conditions are not related to the morphology of the crystalline  $\text{NH}_4\text{MnPO}_4\cdot\text{H}_2\text{O}$  precursor which was recovered from the starting solution by conventional drying.

The results are illustrated schematically in Figure 3. In general, the particle size decreases upon raising the alkalinity of the reactant and increasing the precursor concentration. The latter yields an increase of the number of condensation nuclei, which explains the smaller particle sizes. This behavior is however modified by simultaneous variation of the particles tendency to agglomerate into larger entities, which also depends on both the pH-values of the solutions and the precursor concentrations. Agglomeration is usually favored by attractive van der Waals interactions and prohibited by the electrostatic surface potential. In Figure 3, the region of textured agglomerates is indicated by an orange color. In contrast, the blue color signals the parameter space where individual particle formation is favored.

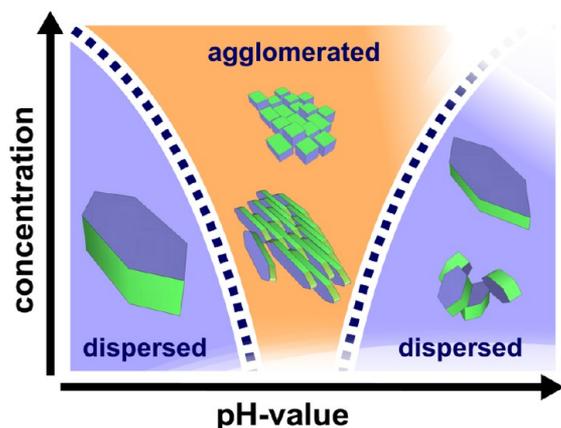
At highest pH, the particles are medium-sized and show low tendency to clot to large structures. Presumably, the strong alkalinity of the solution causes a finite negative surface electrostatic potential preventing contacts of the relatively low concentrated seeds and particles. Straightforwardly, both increasing the precursor concentration and decreasing pH stabilizes the coagulation processes, which is visible in Figure 3.



**Figure 2.** Electron micrographs of  $\text{LiMnPO}_4$  samples, synthesized with three different precursor concentrations and various pH-values (see the text). L: 0.03 mol/L  $\text{Mn}^{2+}$ -ions; M: 0.075 mol/L  $\text{Mn}^{2+}$ -ions; H: 0.13 mol/L  $\text{Mn}^{2+}$ -ions.

In case of neutral surfaces which in the case at hand seems to be realized between pH 8 and 9.5, agglomeration should occur

regardless of the educt concentration (see, e.g., refs 32,33) which is indeed observed in the experiment. Further acidizing is



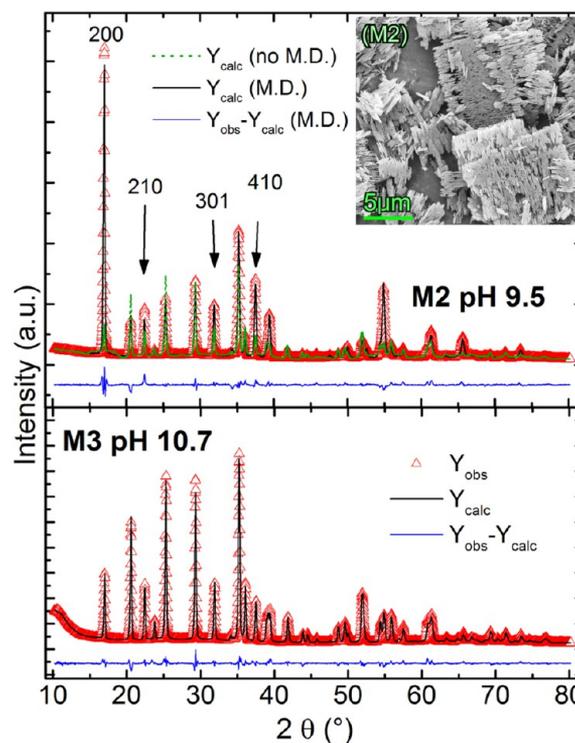
**Figure 3.** Schematic sketch of the pH-value and precursor concentration dependence of particle-size and -agglomeration. The regime of stable dispersion is stained blue, the regime of ordered agglomeration is stained orange.

supposed to generate positively surface charged and hence well dispersed particles. In addition to appropriate charge stabilization in water, a narrow primary particle size distribution is necessary for the formation of ordered agglomerates, too.<sup>34</sup> Indeed, the supporting effect of adapted primary particle size and shape is evident if the strong agglomeration regime in Figure 2 is compared to the region of dispersed particles.

Note that very recently, the isoelectric point in  $\text{LiFePO}_4$  was found at  $\text{pH} = 4.3$ .<sup>35</sup> First, the apparent deviation from  $\text{pH}$  between 8 and 9.5, which is observed in our experiments for  $\text{LiMnPO}_4$ , needs to be qualified by a small uncertainty of the  $\text{pH}$  determination during particle formation. After the syntheses, the  $\text{pH}$ -values were slightly lower (by a maximum of 1) as compared to the educts, which is due to the release of  $\text{NH}_4^+$ -ions from the  $\text{NH}_4\text{MnPO}_4 \cdot \text{H}_2\text{O}$  precipitate. Acidic conditions, however, were never reached in our experiments so that there is a clear contrast to  $\text{LiFePO}_4$ . In iron phosphate, acidic groups resulting from unsaturated metallic cations are supposed to dominate the surface properties in aqueous solution leading to a negative surface charge for  $\text{pH}$ -values even below 3.<sup>36</sup> This coincides with the isoelectric point at acidic  $\text{pH}$ -values. In contrast, our data presented above show that the dominant surface groups of  $\text{LiMnPO}_4$  are less acidic. We suggest that a lower attraction of  $\text{OH}^-$ -ions in  $\text{LiMnPO}_4$  as compared to  $\text{LiFePO}_4$  causes the shift of the isoelectric point to the basic regime, which is consistent with lower acidity of aqueous  $\text{Mn}^{2+}$ -ion as compared to  $\text{Fe}^{2+}$  ( $\text{p}K_a(\text{Mn}^{2+}) = 10.59$ ,  $\text{p}K_a(\text{Fe}^{2+}) = 9.5$ ).

#### Structure Analysis and Preferred Orientation Effects.

A more detailed structural analysis was conducted for two samples (M2, M3) synthesized at a moderate precursor concentration of 0.075 mol/L and at  $\text{pH}$ -values of 9.5 and 10.7, respectively, representing the two different cases of highly agglomerated and dispersed particles. Figure 4 shows the measured XRD patterns of both samples along with the calculated pattern (with pseudo-Voigt profile functions) according to ref 25 including the March-Dollase Model, and the resulting residual. Both patterns exhibit the diffraction peaks characteristic for the orthorhombic  $Pnma$  structure, however huge differences in the relative peak intensities between both samples are visible. While sample M3 shows the pattern of arbitrarily oriented particles expected for dispersed particles, especially the (200), (210), (301), (410), and (610) peaks at



**Figure 4.** Measured and calculated XRD patterns for sample M2 and M3. The labeled peaks for M2 are enlarged as compared to the calculated pattern (green line). This effect is considered by means of the March-Dollase model (black line). Inset: SEM picture of sample carrier after wet preparation process.

$2\theta = 17.0^\circ, 22.4^\circ, 31.8^\circ, 37.5^\circ,$  and  $54.9^\circ$  are enlarged in sample M2 as compared to ref 25. This effect is well-known for oriented powders, and the aberration can be modeled by applying the March-Dollase Model<sup>37</sup> for a preferred powder orientation, with the March-Dollase function:

$$P(r, \alpha) = (r^2 \cos^2(\alpha) + r^{-1} \sin^2(\alpha))^{-3/2} \quad (1)$$

$P(r, \alpha)$  describes the volume fraction of the material oriented at an angle  $\alpha$  with respect to the  $\hat{n}$ -axis, which is normal to a specific crystallographic plane (hkl), and a parameter  $r$ . Refinement of  $r$  in the accordingly modified pattern with the (200), (210), and (301) reflection yields the coefficients listed in Table 1. Considering the (hkl)-planes (410) and (610) does

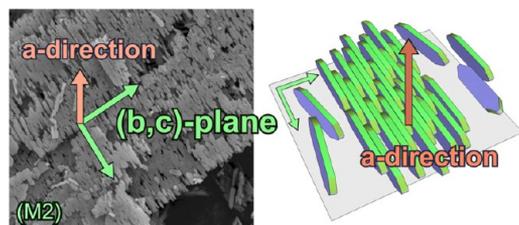
**Table 1.** Calculated March-Dollase Multi-Axial Model Parameters for Sample M2

pref. (hkl)	$\hat{n}$ -fraction	$r$
(200)	0.936	0.503
(210)	0.054	0.441
(301)	0.009	0.308

not further improve the agreement between model and measured data. Note that only the orientation, not the structure, was refined.

The obtained parameters show that the primary crystals are mainly aligned in the (100) plane. This corresponds to the orientation of the crystallographic  $bc$ -plane perpendicular to the plane generated by the X-ray beam and thus parallel to the sample holder. This outcome might be caused by the interplay of two effects, i.e., (1) an anisotropic tendency to

agglomeration of the primary nanocrystals, and (2) the arrangement of the plate-like aggregates of sample M2 parallel to the sample carrier (see the inset of Figure 4). The latter might result from the wet preparation process. In this way, the alignment of the primary particles leads to the fixing of one preferred axis (see Figure 5). The specific orientation of the



**Figure 5.** Relation between agglomeration behavior of primary particles and crystallographic directions. The  $(b,c)$ -surface is green colored, all perpendicular surfaces are blue colored.

crystallographic  $b$ - and  $c$ -directions cannot be deduced from these data. A comparison with electron diffraction data from ref 31, however, suggests that the direction of longest particle dimension corresponds to the  $c$ -axis.

The results imply anisotropic agglomeration tendencies between the  $bc$ -surfaces (no or very low tendency to agglomeration) and the  $ab$ - and  $ac$ -surfaces, respectively (strong agglomeration), and hence indicate different tendencies to charge accretion and thus different repulsive forces. To be specific, the results imply higher charging of the  $bc$ -surface even in the regime of high agglomeration as compared to the other surfaces.

From a structural point of view, the  $bc$ -planes are formed by layers of corner-sharing  $\text{MnO}_6$  octahedra separated by layers containing the  $\text{PO}_4$  tetrahedra and Li-channels, whereas in the  $ab$ - and  $ac$ -planes, only layers containing different polyhedra can be found (for illustration see for example<sup>28</sup>). The higher charging of the  $bc$ -surface might hence result from the presence of just one species at the surface and thus the accretion of only ions with the same sign of charge, e.g., Mn-hydroxocomplexes formed by unsaturated ions in the Mn-oxide layer (acidic behavior) or the formation of hydrogen phosphate with  $\text{PO}_4^{3-}$  groups (basic behavior).

The observed powder XRD orientation effect can be seen to some extent in the patterns of all materials which exhibit the tendency to form ordered agglomerates. In this respect, the analysis of the XRD data confirms the general trends in agglomeration summarized in Figure 3.

Diverse surface functionalities were artificially applied by Xia et al.<sup>38</sup> to Ag-nanocubes dispersed in water. Their observation of self-assembled structures confirms a significant influence of the surface properties on the growth, the texture, and the final size of the agglomerates. Similarly, as outlined above we propose that the formation of diversely shaped and partly oriented agglomerates found in  $\text{LiMnPO}_4$  nanostructures is governed by the particular surface properties. Note that a different mechanism is proposed for  $\text{LiFePO}_4$  microstructures, which have recently been synthesized via a hydrothermal route.<sup>39</sup> While similar to our findings, self-assembled and ordered agglomerates of  $\text{LiFePO}_4$  nanocrystallites are observed, Su et al. emphasizes the relevance of the reaction time and of the template properties of the precursors for the particular

morphology of the aggregates while the specific effect of surface charge is not taken into consideration.

## CONCLUSIONS

We have demonstrated the influence of the fundamental synthesis parameters: pH-value, and precursor concentration in the energy efficient microwave-assisted hydrothermal synthesis process of  $\text{LiMnPO}_4$ . Upon variation of these parameters, we observe regimes where the product consists of well-dispersed particles shaped as hexagonal prisms, the size of which is adjustable from several  $\mu\text{m}$  down to the sub- $\mu\text{m}$  range. In addition, we found a region of parameter space where the particles exhibit a strong agglomerative behavior, thus forming plate-like aggregates. The analysis of the XRD patterns reveals the preferred orientation of the particles and an anisotropic tendency to agglomeration, favoring oriented aggregation in the  $(b,c)$ -plane. These results were used to construct the agglomeration phase diagram, which is discussed with respect to the particles' surface charging behavior. In summary, the appropriate choice of the pH-value and the precursor concentration enables tailoring the size and morphology of  $\text{LiMnPO}_4$  micro- and nanostructure as well as controlling the dispersion or agglomeration.

## ASSOCIATED CONTENT

### Supporting Information

Powder XRD patterns of all samples discussed and SEM images of the recovered precipitates. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Notes

The authors declare no competing financial interest.

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