

## Comparative study on the formation of lithium and sodium manganese phospho-olivines

T. Boyadzhieva, V. Koleva\*, R. Stoyanova

*Institute of General and Inorganic Chemistry, Bulgarian Academy of Sciences,*

*Acad. G. Bonchev Str., Bldg. 11, Sofia 1113, Bulgaria*

Received October 17, 2013; Revised November 25, 2013

The phase formation in the systems  $\text{NH}_4\text{MnPO}_4 \cdot \text{H}_2\text{O}$ - $\text{LiCl}$ - $\text{LiNO}_3$  and  $\text{NH}_4\text{MnPO}_4 \cdot \text{H}_2\text{O}$ - $\text{NaCH}_3\text{COO} \cdot 3\text{H}_2\text{O}$  is systematically investigated in order to obtain at low-temperature olivine-type  $\text{LiMnPO}_4$  and  $\text{NaMnPO}_4$  which are of great interest as cathode materials for lithium and sodium ion batteries. The experimental conditions such as molar ratio between reagents, temperature and reaction time are varied to find the more suitable procedure for the low temperature formation of pure phospho-olivines. It is established that the transformation of the dittmarite precursor into sodium manganese phospho-olivine proceeds between 200-250 °C with participation of large excess of the Na-salt more slowly in comparison with the fast ion exchange of  $\text{NH}_4^+$  for  $\text{Li}^+$  leading to the formation of  $\text{LiMnPO}_4$  for 1.5 h only. Both prepared olivines are well-crystallized and exhibit nano-sized crystallites (50 - 60 nm).

**Keywords:**  $\text{LiMnPO}_4$ ,  $\text{NaMnPO}_4$ , phospho-olivines, Li-ion batteries

### INTRODUCTION

Lithium metal phosphates,  $\text{LiMPO}_4$  (M = Mn, Fe, Co, Ni) with olivine-type structure known as phospho-olivines are amongst the most promising cathode materials for Li-ion batteries due to the high capacity, cyclic stability, tolerance to overcharge, excellent safety and low cost [1-2]. More recently, in response to the current requirements for the development of cheaper "green" batteries the replacement of lithium with sodium becomes very attractive and research on sodium intercalation materials gains an increasing importance [3-4].

While olivine  $\text{LiMPO}_4$  family, and especially  $\text{LiFePO}_4$  and  $\text{LiMnPO}_4$ , is widely studied from different aspects of material science [1,2,5,6], very little work is done on the corresponding sodium analogues [3,7,8]. Owing to the larger ionic size of  $\text{Na}^+$  than  $\text{Li}^+$  the thermodynamically stable  $\text{NaMPO}_4$  compounds do not crystallize in the desired olivine structure: they crystallize in a maricite structure that is electrochemically inactive [3,7,8]. Because of that the synthesis of olivine-type  $\text{NaMPO}_4$  is a great challenge and requires original synthesis approaches.

Regarding  $\text{NaMnPO}_4$  only one report in the literature deals with the preparation of olivine-type

phase [8]. Most recently we have demonstrated that dittmarite-type  $\text{KMnPO}_4 \cdot \text{H}_2\text{O}$  precursor acts as structure and morphology template for low-temperature preparation of nano-sized  $\text{LiMnPO}_4$  and  $\text{NaMnPO}_4$  olivines [9,10].

The present paper is focused on the preparation of olivine-type lithium and sodium manganese phosphates by cation exchange reactions using  $\text{NH}_4\text{MnPO}_4 \cdot \text{H}_2\text{O}$  as a host matrix. The phase composition in the reaction systems  $\text{NH}_4\text{MnPO}_4 \cdot \text{H}_2\text{O}$ - $\text{LiCl}$ - $\text{LiNO}_3$  and  $\text{NH}_4\text{MnPO}_4 \cdot \text{H}_2\text{O}$ - $\text{NaCH}_3\text{COO} \cdot 3\text{H}_2\text{O}$  is studied by X-ray powder diffraction (XRD). Various experimental conditions have been considered, such as molar ratio between the reagents, temperature and reaction time. The specific features of the preparation of  $\text{LiMnPO}_4$  and  $\text{NaMnPO}_4$  from  $\text{NH}_4\text{MnPO}_4 \cdot \text{H}_2\text{O}$  are discussed.

### EXPERIMENTAL

The host matrix  $\text{NH}_4\text{MnPO}_4 \cdot \text{H}_2\text{O}$  is prepared as described elsewhere [11]. The cation exchange of  $\text{NH}_4^+$  for  $\text{Li}^+$  and  $\text{Na}^+$  is carried out using eutectic composition  $\text{LiCl}$ - $\text{LiNO}_3$  (0.12:0.88 mole ratio) and  $\text{NaCH}_3\text{COO} \cdot 3\text{H}_2\text{O}$ , respectively, as lithium and sodium reagents are taken in excess. The synthetic procedure is same for both systems and it is analogical to that applied in the case of  $\text{KMnPO}_4$ .

\* To whom all correspondence should be sent:

E-mail: vkoleva@svr.igic.bas.bg

H<sub>2</sub>O [9,10]. For the lithium system the experiments are carried out at 200 and 270 °C, whereas for the sodium system a broader temperature interval from 75 to 250 °C is explored. The molar ratio between NH<sub>4</sub>MnPO<sub>4</sub>·H<sub>2</sub>O and Li-salt (accordingly Na-salt) is varied between 1:2 and 1:12. The reaction time is also varied from 1.5 to 24 h.

The XRD patterns are recorded on a Bruker Advance 8 diffractometer using CuKα radiation. The lattice parameters are determined by WinPlotr programme. The crystallite sizes are calculated by the Scherrer equation as the instrumental broadening is taken into account. The line width is determined by profile analysis (WinPlotr programme). The TG-DTA analysis of NH<sub>4</sub>MnPO<sub>4</sub>·H<sub>2</sub>O is performed using LABSYS™ Evo apparatus (SETARAM) in an argon flow at a heating rate of 10 °C/min.

## RESULTS AND DISCUSSION

NH<sub>4</sub>MnPO<sub>4</sub>·H<sub>2</sub>O belongs to the dittmarite family which is characterized by a layer structure consisting of M<sup>2+</sup>-PO<sub>4</sub> sheets separated by M<sup>+</sup> ions [12]. Due to the remarkable structural similarity in the topology of the M<sup>2+</sup>-PO<sub>4</sub> layers between dittmarite and olivine structures, the dittmarites are particularly suitable as precursors in cation exchange reaction [8-10,13].

Since the dehydration process is very essential for the transformation of the dittmarite into olivine structure [9,10] we have analyzed the thermal behaviour of the NH<sub>4</sub>MnPO<sub>4</sub>·H<sub>2</sub>O precursor (Fig. 1). It is stable up to 135 °C when a complex decomposition with simultaneous release of H<sub>2</sub>O and NH<sub>3</sub> takes place resulting in the formation of MnHPO<sub>4</sub> around 300 °C (18.72 % mass loss vs calculated 18.92 %). Above 350 °C MnHPO<sub>4</sub>

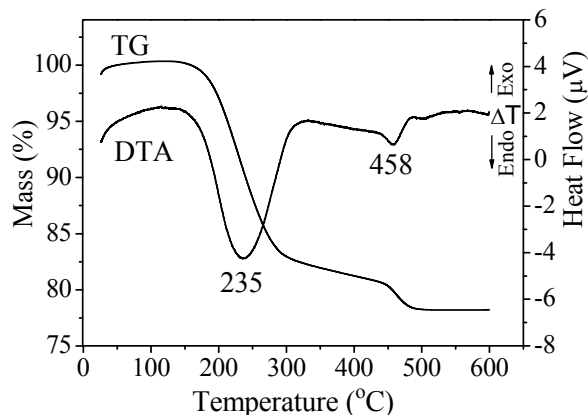


Fig. 1. TG- and DTA curves for NH<sub>4</sub>MnPO<sub>4</sub>·H<sub>2</sub>O.

undergoes an inter-molecular dehydration to Mn<sub>2</sub>P<sub>2</sub>O<sub>7</sub> (5.56 % mass loss vs calculated 5.96 %)

in accordance with the XRD data of Wenwei et al. [14]. The two endothermic effects at 235 and 458 °C correspond to the above processes.

The major advantage of the reactions in molten salts is the ability to run the process at low-temperature which is favorable for the formation of small particles as well as the synthesis process is less expensive. Eutectic LiCl-LiNO<sub>3</sub> with a low melting point of 270 °C is very suitable for cation exchange reactions for Li<sup>+</sup>. To facilitate the ion-exchange reaction, the molten salts are usually taken in large (e.g. tenfold) excess. Our first experiment performed with tenfold excess of Li-eutectic (1:10 mole ratio) at 270 °C for 6h (Fig. 2) shows that the reaction product comprises approximately 90 % olivine phase, 10 % Li<sub>3</sub>PO<sub>4</sub> (PDF 71-1528) and small amount of an unidentified phase. Evidently, the high concentration of lithium

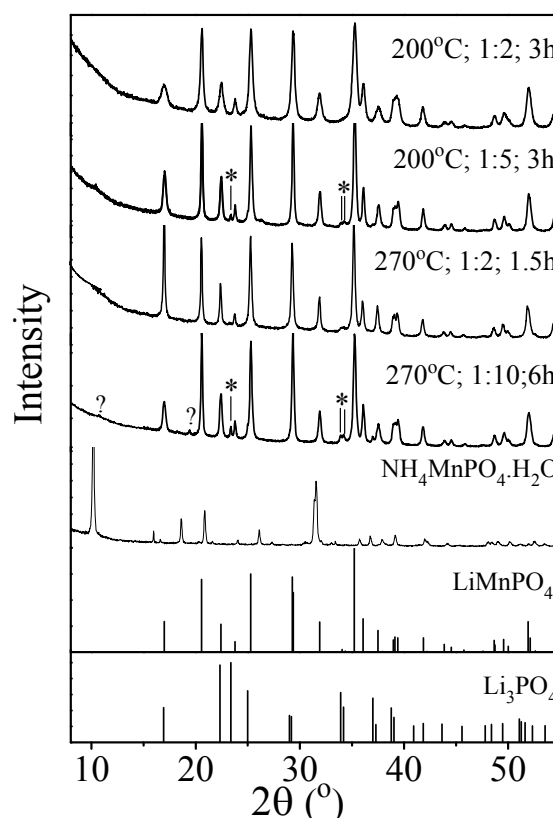


Fig. 2. XRD patterns of the reaction product in NH<sub>4</sub>MnPO<sub>4</sub>·H<sub>2</sub>O–LiCl–LiNO<sub>3</sub> system at different experimental conditions (\* denotes Li<sub>3</sub>PO<sub>4</sub>; ? denotes an unidentified impurity).

ions promotes competitive reaction of decomposition of the dittmarite precursor.

The drastic reduction of the amount of the Li-eutectic and reaction time (1:2, 90 min) results in a fast formation of LiMnPO<sub>4</sub> free of impurities (Fig. 2). Successful experiments are also performed at

200 °C i.e. at a temperature below the melting point of the Li-eutectic (Fig.2). Pure  $\text{LiMnPO}_4$  is obtained at a mole ratio 1:2 for 3h, while very small amount of  $\text{Li}_3\text{PO}_4$  (below 1 %) is detected with the larger excess (1:5) of the Li-eutectic (Fig. 2).

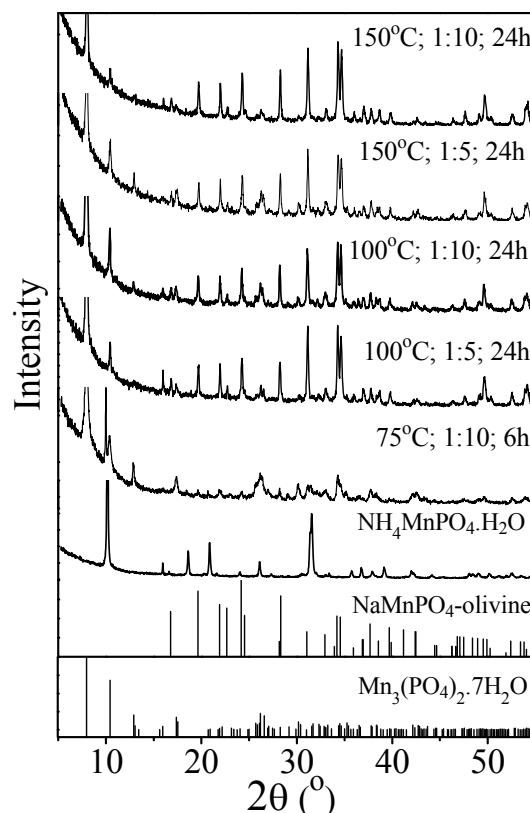
It is clear that formation of the olivine phase takes place at temperatures where the parent  $\text{NH}_4$ -precursor should decompose to  $\text{MnHPO}_4$  (Fig. 1). The absence of any pyrophosphate phases is a further support that the ion exchange of  $\text{NH}_4^+$  for  $\text{Li}^+$  occurs very fast in the framework of the dittmarite structure, and thus the decomposition of the precursor is prevented. The ion exchange is immediately followed by the  $\text{H}_2\text{O}$  release and the transformation of the dittmarite structure into olivine structure is accomplished.

The prepared  $\text{LiMnPO}_4$  (Fig. 2) display a good crystallinity irrespective of the low synthesis temperatures and short reaction time. The lattice parameters do not depend on the temperature of formation ( $a = 10.4429(4) \text{ \AA}$ ,  $b = 6.0879(2) \text{ \AA}$ ,  $c = 4.7480(2) \text{ \AA}$ ) and coincide well with the reported in the literature [9,13,15].

Ion-exchange of  $\text{NH}_4^+$  for  $\text{Na}^+$  is performed with  $\text{NaCH}_3\text{COO} \cdot 3\text{H}_2\text{O}$  having very low melting point of 58 °C. At dynamic conditions (heating with 10 °C/min) Liptay reported [16] that at about 65-70 °C the salt undergoes an incongruent melting, followed by a complete dehydration at 200-220 °C. The anhydrous sodium acetate melts at 324 °C [16]. Considering these data the first experiment is performed at 75 °C using 1:10 mole ratio and a reasonable reaction time of 6h. At these conditions (Fig. 3) the reaction product comprises a mixture of a main component (about 60 %)  $\text{Mn}_3(\text{PO}_4)_2 \cdot 7\text{H}_2\text{O}$  (PDF 84-1160), unreacted precursor (about 20 %) and small amount (about 15-20 %) of target olivine  $\text{NaMnPO}_4$  (PDF 74-386). Taking into account that the parent  $\text{NH}_4$ -precursor is thermally stable at 75 °C (Fig. 1) the presence of  $\text{Mn}_3(\text{PO}_4)_2 \cdot 7\text{H}_2\text{O}$  can be explained by the precursor decomposition under the influence of the high concentration of  $\text{Na}^+$ . Evidently, the ion exchange reaction and the decomposition reaction are competitive reactions and at the above synthesis conditions the latter predominates over the former. To enhance the rate of the ion-exchange reaction the next experiments are performed at higher temperatures (between 100 and 250 °C), longer reaction times and varying the excess of  $\text{NaCH}_3\text{COO} \cdot 3\text{H}_2\text{O}$  (Figs. 3 and 4).

Unreacted precursor is not observed at 100 °C and between 100 and 150 °C the reaction product is biphasic consisting of  $\text{Mn}_3(\text{PO}_4)_2 \cdot 7\text{H}_2\text{O}$  (still main

component) and  $\text{NaMnPO}_4$  (Fig. 3). At 150 °C the amount of the olivine phase reaches to 40 %. It is worth noting that our results on the phase composition between 75 and 100 °C differ considerably from these of Nazar et al. [8], who reported for the preparation of pure olivine  $\text{NaMnPO}_4$  between 65 and 100 °C using the same reaction reagents (no experimental details were supplied).

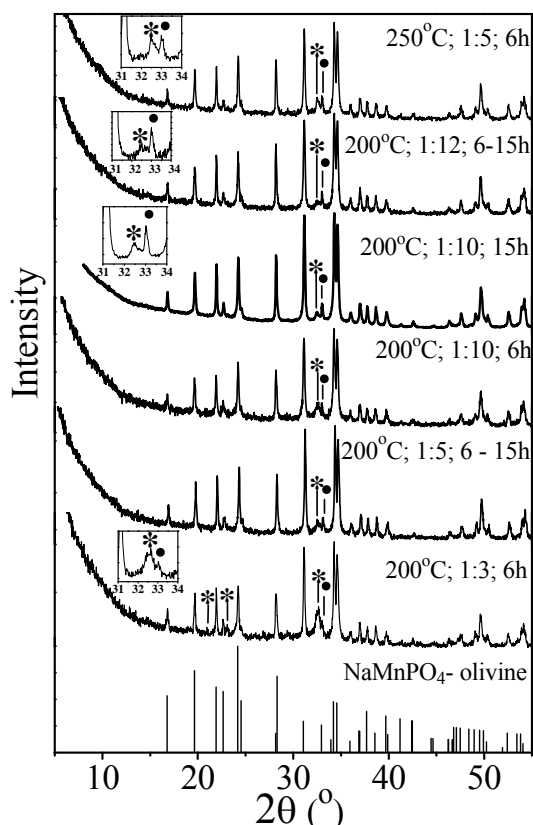


**Fig. 3.** XRD patterns of the reaction product in  $\text{NH}_4\text{MnPO}_4 \cdot \text{H}_2\text{O} - \text{NaCH}_3\text{COO} \cdot 3\text{H}_2\text{O}$  system at temperatures between 75 and 150 °C .

At 200 °C the target olivine phase becomes the main component in the system (Fig. 4).  $\text{Mn}_3(\text{PO}_4)_2 \cdot 7\text{H}_2\text{O}$  is now absent, but minor quantity of another impurity (most probably  $\text{NaMn}_3(\text{PO}_4)(\text{HPO}_4)_2$  (PDF 83-329)) is also observed.

The inset on Fig. 4 compares the intensity of the peak due to the impurity with the intensity of the nearest olivine peak at different experimental conditions. The comparison clearly shows that the quantity of the impurity decreases with the increase in the excess of  $\text{NaCH}_3\text{COO} \cdot 3\text{H}_2\text{O}$  and the reaction time. Best results regarding the purity of olivine  $\text{NaMnPO}_4$  are achieved at 1:10 mole ratio for 15 h as well as at 1:12 mole ratio for 6h (same for 15 h).

The level of the impurity in these cases is around 5 %.



**Fig. 4.** XRD patterns of the products in  $\text{NH}_4\text{MnPO}_4 \cdot \text{H}_2\text{O}$  –  $\text{NaCH}_3\text{COO} \cdot 3\text{H}_2\text{O}$  system at temperatures of 200-250 °C (\* denotes the impurity; • denotes the nearest olivine peak).

The prepared olivine  $\text{NaMnPO}_4$  at 200 °C is well-crystallized (Fig. 4) and the unit cell parameters ( $a = 10.5275(5)$  Å,  $b = 6.3232(3)$  Å,  $c = 4.9843(3)$  Å) coincides well with the reported for  $\text{NaFe}_{0.07}\text{Mn}_{0.93}\text{PO}_4$  (mineral natrophilite having olivine structure) [17] as well as with these for  $\text{NaMnPO}_4$  prepared by us from  $\text{KMnPO}_4 \cdot \text{H}_2\text{O}$  [10].

Regarding the preparation of  $\text{LiMnPO}_4$  and  $\text{NaMnPO}_4$  olivines from  $\text{NH}_4\text{MnPO}_4 \cdot \text{H}_2\text{O}$ , it appears that the synthesis of  $\text{LiMnPO}_4$  proceeds by using a small excess of the Li-reagent (not more than twofold excess) and short reaction time (up to 3h), while a large excess of the Na-reagent (tenfold and more) and longer reaction time (15 h) are needed for the synthesis of olivine  $\text{NaMnPO}_4$ : The difference in the formation of lithium and sodium analogues can be related with the hindered diffusion of the larger  $\text{Na}^+$  ions in comparison with the fast mobility of the smaller  $\text{Li}^+$  ions at same temperature (e.g. 200 °C). However, because of the low synthesis temperature (200 °C) the crystallite sizes of both sodium and lithium phospho-olivines are in the nano-scale region: The average crystallite

size calculated from the line broadening of six diffraction peaks from the 16–35 ° ( $2\theta$ ) range is 47 nm for  $\text{LiMnPO}_4$  and 61 nm for  $\text{NaMnPO}_4$ . The larger crystallite size for sodium phospho-olivine could be explained by the prolonged heating at 200 °C that favors the crystallite growth.

## CONCLUSION

Nano-crystalline olivine-type  $\text{LiMnPO}_4$  and  $\text{NaMnPO}_4$  are prepared at low temperatures (i.e. around 200 °C). It has been demonstrated that dittmarite-type compound  $\text{NH}_4\text{MnPO}_4 \cdot \text{H}_2\text{O}$  is a suitable structure template for the synthesis of lithium and sodium phospho-olivines, which are promising cathode materials in lithium and sodium ion batteries.

**Acknowledgments:** This work was supported by European Social Fund (Grant BG051PO001-3.3.06-0050) and National Centre for New Materials UNION (Contract No DCVP-02/2/2009).

## REFERENCES

1. B.L. Ellis, K.T. Lee, L.F. Nazar, *Chem. Mater.*, **22**, 691 (2010).
2. M.S. Whittingham, *Chem. Rev.*, **104**, 4271 (2004).
3. B.L. Ellis, L.F. Nazar, *Curr. Opin. Solid State Mater. Sci.*, **16**, 168 (2012).
4. N. Yabuuchi, M. Kajiyama, J. Iwatate, H. Nishikawa, S. Hitomi, R. Okuyama, R. Usui, Y. Yamada, S. Komaba, *Nat. Mater.*, **11**, 512 (2012).
5. M.S. Whittingham, Y. Song, S. Lutta, P.Y. Zavalij, N. Chernova, *J. Mat. Chem.*, **15**, 3362 (2005).
6. K. Zaghib, A. Mauger, C.M. Julien, *J. Solid State Electrochem.*, **16**, 835 (2012).
7. K. Zaghib, J. Trottier, P. Hovington, F. Brochu, A. Guerfi, A. Mauger, C.M. Julien, *J. Power Sources*, **196**, 9612 (2011).
8. K.T. Lee, T.N. Ramesh, F. Nan, G. Botton, L.F. Nazar, *Chem. Mater.*, **23**, 3593 (2011).
9. V. Koleva, E. Zhecheva, R. Stoyanova, *Dalton Trans.*, **40**, 7385 (2011).
10. V. Koleva, T. Boyadzhieva, E. Zhecheva, D. Nihtianova, S. Simova, G. Tyuliev, R. Stoyanova, *Cryst. Eng. Comm.*, **15**, 9080 (2013).
11. V.G. Koleva, *Spectrochim. Acta*, **66A**, 413 (2007).
12. G. Carling, P. Day, D. Visser, *Inorg. Chem.*, **34**, 3917 (1995).
13. N. Bramnik, H. Ehrenberg, *J. Alloys Compd.*, **464**, 259 (2008).
14. W. Wenwei, F. Yanjin, W. Xuehang, L. Sen, L. Shushu, *J. Phys. Chem. Solids*, **70**, 584 (2009).
15. V.A. Strel'tsov, E.L. Belokoneva, V.G. Tsirelson, N.K. Hansen, *Acta Cryst.*, **49B**, 147 (1993).
16. Liptay, Atlas of Thermoanalytical curves, Vol. 1, Akademiai Kiado, Budapest, 1971
17. P.B. Moore, *Am. Mineral.*, **57**, 1333 (1972).



СРАВНИТЕЛНО ИЗСЛЕДВАНЕ НА ОБРАЗУВАНЕТО НА  
ЛИТИЕВО-МАНГАНОВ И НАТРИЕВО-МАНГАНОВ ФОСФО-ОЛИВИНИ

Т. Бояджиева, В. Колева, Р. Стоянова

*Институт по обща и неорганична химия, Българска академия на науките,*

*1113 София, България*

Постъпила на 17 октомври 2013 г.; коригирана на 25 ноември, 2013 г.

(Резюме)

Фазообразуването в системите  $\text{NH}_4\text{MnPO}_4 \cdot \text{H}_2\text{O} - \text{LiCl} - \text{LiNO}_3$  и  $\text{NH}_4\text{MnPO}_4 \cdot \text{H}_2\text{O} - \text{NaCH}_3\text{COO} \cdot 3\text{H}_2\text{O}$  е систематично изучено с цел да се получат при ниска температура оливинов-тип  $\text{LiMnPO}_4$  и  $\text{NaMnPO}_4$ , които представляват интерес като катодни материали за литиево- и натриево-йонни батерии. Варирани са редица експериментални параметри като молно отношение между реагентите, температура и реакционно време, за да се намерят най-подходящите условия за ниско температурно образуване на чисти фосфо-оливини. Установено е, че трансформирането на дитмаритния прекурсор в натриево-манганов фосфо-оливин протича между 200 и 250 °C в присъствие на голям излишък от натриева сол много по-бавно в сравнение с бързия йонен обмен на  $\text{NH}_4^+$  с  $\text{Li}^+$  йони, водещ до образуване на  $\text{LiMnPO}_4$  само за 90 мин. Получените фосфо-оливини се характеризират с добра кристалност и нано-размерни кристали (50-60 nm).