# Syntheses, Structures, Anomalous Phase Transition and Optical Properties of Two New Polymorphic $\alpha$- and $\beta$-$LiMoPO_6$

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**Table S1.** Atomic Coordinates and Equivalent Isotropic Displacement parameters for $\alpha$- and $\beta$-$LiMoPO_6$.

$\alpha$-$LiMoPO_6$

| Atom | x | y | z | U(eq) | BVS |
|---|---|---|---|---|---|
| Li(1) | 6682(3) | 3841(4) | 6599(4) | 21(1) | 1.07 |
| Mo(1) | 6198(1) | 2505(1) | 302(1) | 9(1) | 6.21 |
| P(1) | 6449(1) | 1247(1) | 4044(1) | 8(1) | 5.12 |
| O(1) | 7114(1) | 2330(2) | 5084(2) | 14(1) | 2.11 |
| O(2) | 6808(1) | 1433(2) | 2389(2) | 15(1) | 2.02 |
| O(3) | 6617(1) | -331(2) | 4570(2) | 22(1) | 2.00 |
| O(4) | 5235(1) | 1718(2) | 4209(2) | 19(1) | 2.21 |
| O(5) | 5973(1) | 3072(2) | -1520(2) | 23(1) | 2.03 |
| O(6) | 6106(1) | 4158(2) | 1260(2) | 26(1) | 2.02 |

$\beta$-$LiMoPO_6$.

| Atom | x | y | z | U(eq) | BVS |
|---|---|---|---|---|---|
| Li(1) | 5471(13) | 1787(10) | 4597(7) | 39(2) | 0.98 |
| Mo(1) | 2622(1) | -326(1) | 1953(1) | 7(1) | 6.01 |
| P(1) | 7549(1) | 475(1) | 1644(1) | 6(1) | 4.96 |
| O(1) | 5710(3) | -861(3) | 1579(2) | 9(1) | 2.02 |
| O(2) | 9587(3) | -619(3) | 1998(2) | 11(1) | 2.10 |
| O(3) | 7651(3) | 1408(3) | 200(2) | 10(1) | 1.99 |
| O(4) | 3350(3) | -1(3) | 3752(2) | 13(1) | 2.01 |
| O(5) | 2686(3) | 1714(3) | 1252(2) | 14(1) | 1.86 |
| O(6) | 7273(3) | 1821(3) | 2826(2) | 10(1) | 1.95 |

**Table S2.** Selected Bond Distances (Å) and Angles (°) for $\alpha$- and $\beta$-$LiMoPO_6$.

| $\alpha$-$LiMoPO_6$ | | | |
|---|---|---|---|
| Distances (Å) | | | |
| Mo(1)-O(5) | 1.6929(15) | P(2)-O(2) | 1.5192(13) |
| Mo(1)-O(6) | 1.7001(15) | P(2)-O(4) | 1.5360(13) |
| Mo(1)-O(4)#1 | 1.9205(13) | P(2)-O(1) | 1.5528(14) |
| Mo(1)-O(1)#2 | 2.0593(14) | O(1)-Mo(1)#4 | 2.0593(14) |
| Mo(1)-O(3)#3 | 2.1055(14) | O(3)-Mo(1)#5 | 2.1055(14) |
| Mo(1)-O(2) | 2.1878(13) | O(4)-Mo(1)#1 | 1.9205(13) |
| P(2)-O(3) | 1.4952(14) | | |
| Angles (°) | | | |
| O(5)-Mo(1)-O(6) | 101.13(9) | O(6)-Mo(1)-O(2) | 89.50(7) |
| O(5)-Mo(1)-O(4)#1 | 99.96(7) | O(4)#1-Mo(1)-O(2) | 87.71(6) |
| O(6)-Mo(1)-O(4)#1 | 98.57(7) | O(1)#2-Mo(1)-O(2) | 76.89(5) |
| O(5)-Mo(1)-O(1)#2 | 92.94(6) | O(3)#3-Mo(1)-O(2) | 76.62(6) |
| O(6)-Mo(1)-O(1)#2 | 92.77(7) | O(3)-P(2)-O(2) | 110.91(8) |
| O(4)#1-Mo(1)-O(1)#2 | 160.80(6) | O(3)-P(2)-O(4) | 111.09(9) |
| O(5)-Mo(1)-O(3)#3 | 91.64(8) | O(2)-P(2)-O(4) | 109.51(8) |
| O(6)-Mo(1)-O(3)#3 | 164.86(7) | O(3)-P(2)-O(1) | 109.57(9) |
| O(4)#1-Mo(1)-O(3)#3 | 87.05(6) | O(2)-P(2)-O(1) | 109.90(8) |
| O(1)#2-Mo(1)-O(3)#3 | 78.35(6) | O(4)-P(2)-O(1) | 105.74(8) |
| O(5)-Mo(1)-O(2) | 165.72(7) | | |
| $\beta$-$LiMoPO_6$. | | | |
| Distances (Å) | | | |
| Mo(1)-O(5) | 1.684(2) | P(1)-O(3) | 1.5305(19) |
| Mo(1)-O(4) | 1.726(2) | P(1)-O(1) | 1.544(2) |
| Mo(1)-O(2)#4 | 1.9422(19) | P(1)-O(2) | 1.550(2) |
| Mo(1)-O(1) | 2.0573(18) | O(2)-Mo(1)#8 | 1.9422(19) |
| Mo(1)-O(3)#5 | 2.1662(18) | O(3)-Mo(1)#5 | 2.1662(18) |
| Mo(1)-O(6)#6 | 2.177(2 | O(6)-Mo(1)#3 | 2.177(2) |
| P(1)-O(6) | 1.525(2) | | |
| Angles (°) | | | |
| O(5)-Mo(1)-O(4) | 103.54(10) | O(4)-Mo(1)-O(6)#6 | 92.66(9) |
| O(5)-Mo(1)-O(2)#4 | 99.69(9) | O(2)#4-Mo(1)-O(6)#6 | 84.66(8 |
| O(4)-Mo(1)-O(2)#4 | 100.63(9) | O(1)-Mo(1)-O(6)#6 | 78.30(7) |
| O(5)-Mo(1)-O(1) | 93.62(9) | O(3)#5-Mo(1)-O(6)#6 | 73.15(7) |
| O(4)-Mo(1)-O(1) | 90.49(9) | O(6)-P(1)-O(3) | 110.09(11) |
| O(2)#4-Mo(1)-O(1) | 160.07(8) | O(6)-P(1)-O(1) | 109.83(11) |
| O(5)-Mo(1)-O(3)#5 | 89.47(9) | O(3)-P(1)-O(1) | 110.74(11) |
| O(4)-Mo(1)-O(3)#5 | 162.59(9) | O(6)-P(1)-O(2) | 110.28(11) |
| O(2)#4-Mo(1)-O(3)#5 | 88.30(8) | O(3)-P(1)-O(2) | 110.08(11) |
| O(1)-Mo(1)-O(3)#5 | 76.99(7) | O(1)-P(1)-O(2) | 105.74(11) |
| O(5)-Mo(1)-O(6)#6 | 162.03(9) | | |

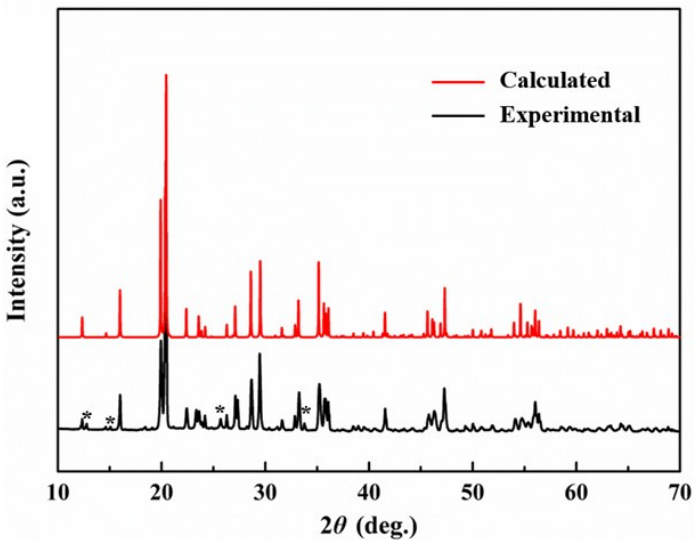


**Figure S1.** Powder-XRD patterns of $\alpha$-$LiMoPO_6$. (* = $MoO_3$)

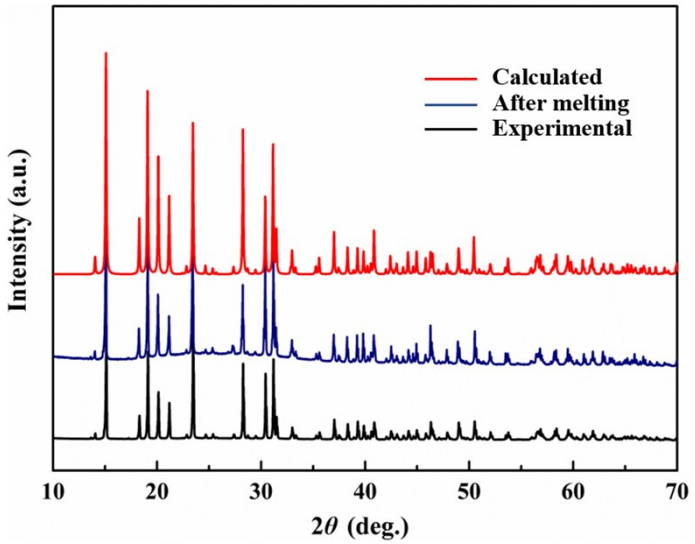


**Figure S2.** Powder-XRD patterns of $\beta$-$LiMoPO_6$.

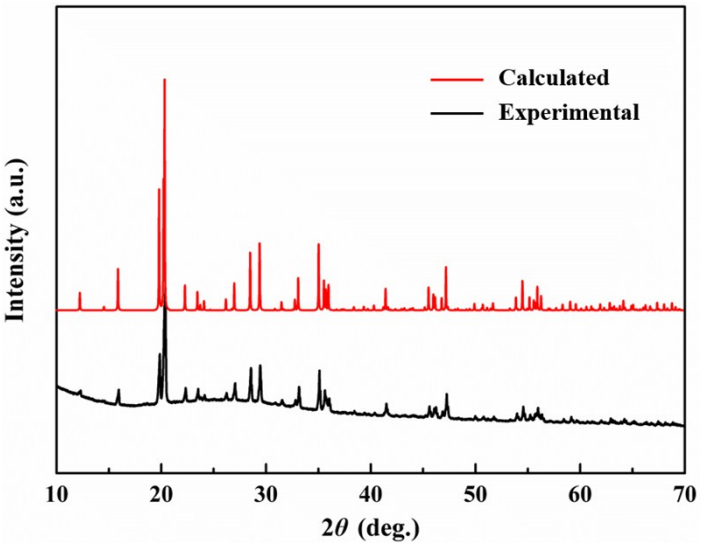


**Figure S3.** Powder-XRD patterns of pure $\alpha$-$LiMoPO_6$.

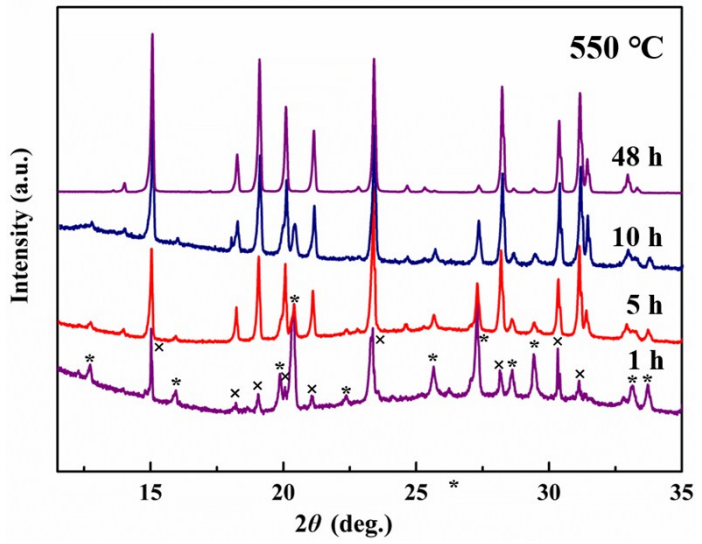


**Figure S4.** Thermal evolution of the PXRD patterns showing the role of reaction time (1 - 48 h) in the progression of the phase transformation from $\alpha$-$LiMoPO_6$ to $\beta$-$LiMoPO_6$. ( $*$ = $\alpha$-$LiMoPO_6$; × = $\beta$-$LiMoPO_6$).

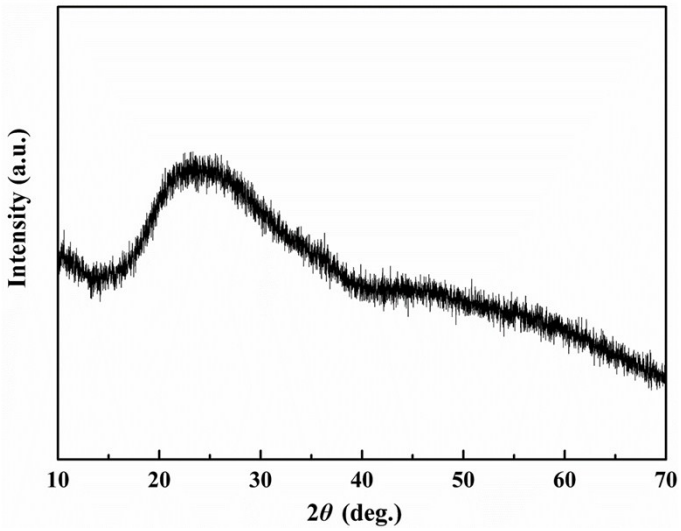


**Figure S5.** The XRD patterns of residues after TG/DSC.

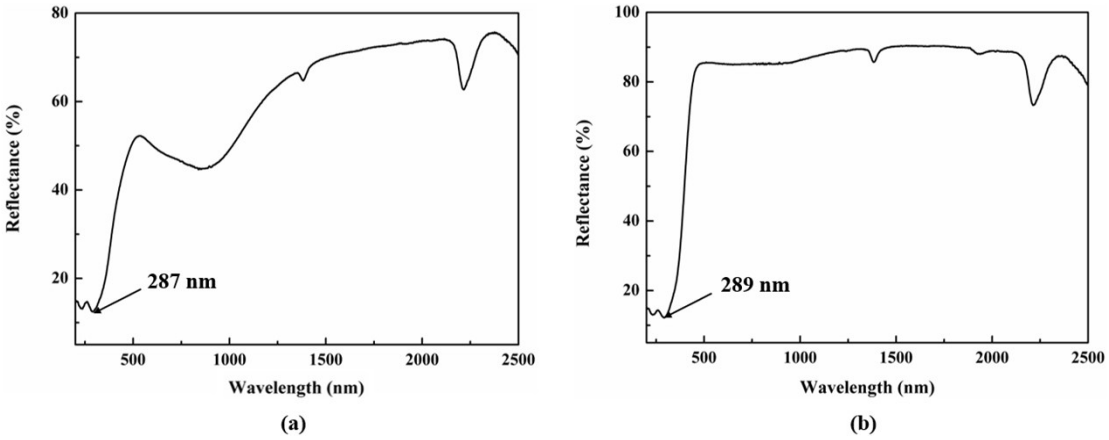


**Figure S6.** UV−VIS−NIR di□use reflectance spectra of $\alpha$- and $\beta$-$LiMoPO_6$.