



## Syntheses, crystal structures, and characterizations of $\text{LiM}(\text{PO}_3)_4$ ( $M = \text{Y}, \text{Dy}$ )

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### ABSTRACT

Two tertiary rare earth polyphosphates, namely,  $\text{LiM}(\text{PO}_3)_4$  ( $M = \text{Y}, \text{Dy}$ ), have been synthesized by the solid-state reaction and structurally established by single-crystal X-ray diffraction (XRD). The two compounds crystallize in monoclinic space group  $C2/c$  and  $Z = 4$ . They are isostructural and the structures feature interconnected Y–Li straight chains and  $[\text{PO}_4]^{3-}$  wavy chains. Additionally, the calculations of band structure, density of states of  $\text{LiY}(\text{PO}_3)_4$  were performed with the density functional theoretical (DFT) method and the optical properties of  $\text{LiDy}(\text{PO}_3)_4$  were investigated in terms of emission spectra.

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## 1. Introduction

In recent years, the chemistry of alkali rare earth polyphosphate have been studied mainly due to their rich structural chemistry and interesting physical and chemical properties such as high luminescence efficiency [1–6]. For example,  $\text{KGdP}_4\text{O}_{12}$  [7],  $\text{KNd}(\text{PO}_3)_4$  [8], and  $\text{LiLn}(\text{PO}_3)_4$  ( $\text{Ln} = \text{La}, \text{Nd}, \text{Eu}, \text{Gd}, \text{Tb}, \text{Er}, \text{and Yb}$ ) [9–13], have been reported recently. Furthermore, their chemical and thermal stability ensures the feasibility of the industrial applications.

But until now, rare earth polyphosphates containing lithium have not been fully explored in the system. In order to enrich this family of  $\text{M}^{\text{I}}\text{M}^{\text{III}}(\text{PO}_3)_4$  compounds, we investigate the  $\text{Li}_2\text{O}-\text{M}^{\text{III}}\text{O}_3-\text{P}_2\text{O}_5$  ( $M = \text{Y}, \text{Dy}$ ) ternary system, and finally the  $\text{LiM}(\text{PO}_3)_4$  ( $M = \text{Y}, \text{Dy}$ ) single crystals were successfully determined by X-ray diffraction. They are isostructural with  $\text{LiLn}(\text{PO}_3)_4$  ( $\text{Ln} = \text{La}, \text{Nd}, \text{Eu}, \text{Gd}, \text{Tb}, \text{Er}, \text{and Yb}$ ) [9–13] and their structure can be simply described as a three-dimensional (3D) framework made up from 1D  $(\text{PO}_4)^{3-}$  wavy chains and 1D Y–Li chains parallel to  $b$ -axis. In addition, the band structure, density of states (DOS), and dielectric constant of  $\text{LiY}(\text{PO}_3)_4$  are investigated by theoretical calculations with the DFT method.

## 2. Experimental and computational procedures

### 2.1. Synthesis

Single crystals of  $\text{LiM}(\text{PO}_3)_4$  ( $M = \text{Y}, \text{Dy}$ ) were prepared by the high temperature solution reaction. All reagents were purchased commercially and used without further purification. The starting

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materials containing analytical reagent  $\text{Li}_2\text{CO}_3$ ,  $\text{M}_2\text{O}_3$  ( $M = \text{Y}, \text{Dy}$ ), and  $\text{NH}_4\text{H}_2\text{PO}_4$  were weighed in the molar ratio of  $\text{Li}/\text{M}/\text{P} = 7/1/10$ . Starting mixtures were finely ground in an agate mortar to ensure the best homogeneity and reactivity, then placed in a platinum crucible and heated at 673 K for 4 h in order to decompose  $\text{NH}_4\text{H}_2\text{PO}_4$  and  $\text{Li}_2\text{CO}_3$ . Afterwards, the mixtures were reground and heated to 1073 K for 20 h. Finally, the temperature was lowered to 873 K at a rate of 4 K/h and air-quenched to room temperature. A few colorless needle-like crystals were obtained from the melt of the mixture.

After crystal structure determination, polycrystalline samples of these compounds were synthesized by solid-state reactions of stoichiometric amounts of analytical reagents  $\text{Li}_2\text{CO}_3$ ,  $\text{M}_2\text{O}_3$  ( $M = \text{Y}, \text{Dy}$ ), and  $\text{NH}_4\text{H}_2\text{PO}_4$ . The pulverous mixtures were allowed to react at 973 K for 120 h with several intermediate grindings in an open Pt crucible.

### 2.2. Crystal structure determination and spectral measurements

Single crystals of  $\text{LiM}(\text{PO}_3)_4$  ( $M = \text{Y}, \text{Dy}$ ) having dimensions  $0.30 \times 0.30 \times 0.20 \text{ mm}^3$  ( $\text{LiY}(\text{PO}_3)_4$ ) and  $0.15 \times 0.15 \times 0.10 \text{ mm}^3$  ( $\text{LiDy}(\text{PO}_3)_4$ ) were selected for X-ray diffraction determination. The diffraction data for  $\text{LiY}(\text{PO}_3)_4$  were collected on a Rigaku Mercury CCD diffractometer with graphite-monochromated  $\text{Mo-K}\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) using the  $\omega$  scan mode at the temperature of 293 K, and for  $\text{LiDy}(\text{PO}_3)_4$  were collected on a Siemens SMART CCD diffractometer with graphite-monochromated  $\text{Mo-K}\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) using the  $\omega/2\theta$  scan mode at the temperature of 293 K. The data set was corrected for Lorentz factor, polarization, air absorption and absorption due to variations in the path length through the detector faceplate.

The structures were solved using direct methods and refined on  $F^2$  by the full-matrix least-squares method with the SHELX-97 program package. The positions of the Y and Dy atoms were refined by the application of the direct method, and the remaining atoms were located in succeeding difference Fourier synthesis. All atomic sites for  $\text{LiM}(\text{PO}_3)_4$  ( $M = \text{Y, Dy}$ ) were fully occupied according to the site occupancy refinements and no abnormal behaviors were found for their thermal parameters. Table 1 lists details of cell parameters, data acquisition, and structure solution. The atomic coordinates and thermal parameters are listed in Table 2. Selected bond distances and angles are given in Table 3. Further details on crystallographic studies are given as Supporting Information.

The samples used for spectral measurements were polycrystalline powder synthesized by solid-state reactions. To give evidence that they contain pure phase of sample, we measured the powder XRD patterns of  $\text{LiM}(\text{PO}_3)_4$  ( $M = \text{Y, Dy}$ ) using RIGAKU DMAX2500 diffractometer with  $\text{CuK}\alpha$  radiation (step size of  $0.05^\circ$  and range  $2\theta = 10 - 65^\circ$ ). The powder XRD patterns of  $\text{LiM}(\text{PO}_3)_4$  ( $M = \text{Y, Dy}$ ) which compare with the simulated ones confirm the monophasic nature of the prepared samples. The powder XRD patterns of tile compounds are given as Support Information. The emission spectra were measured with an FLS920 time-resolved fluorescence spectrometer using an Xe lamp at room temperature.

### 2.3. Computational description

The crystallographic data of  $\text{LiY}(\text{PO}_3)_4$  determined by X-ray diffraction was used to calculate electronic band structures by the density functional theory (DFT) using one of the three nonlocal gradient-corrected exchange-correlation functional (GGA-PBE) and performed with the CASTEP code [14,15], which uses a plane wave basis set for the valence electrons and norm-conserving pseudopotential for the core states. The number of plane waves included in the basis is determined by a cutoff energy of 500 eV and the

**Table 1**  
Crystal data and structure refinements for  $\text{LiM}(\text{PO}_3)_4$  ( $M = \text{Y, Dy}$ )

	$\text{LiY}(\text{PO}_3)_4$	$\text{LiDy}(\text{PO}_3)_4$
Formula	$\text{LiY}(\text{PO}_3)_4$	$\text{LiDy}(\text{PO}_3)_4$
Formula weigh ( $\text{g mol}^{-1}$ )	411.73	485.32
Wavelength ( $\text{\AA}$ )	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic
Space group	$C2/c$	$C2/c$
<i>Unit cell dimensions</i>		
<i>a</i>	16.236(5)	16.2600(14)
<i>b</i>	7.0183(16)	7.0259(6)
<i>c</i>	9.548(3)	9.5783(8)
$\beta$	125.98(3)	126.0180(10)
Volume, <i>Z</i>	880.4(4), 4	885.05(13), 4
$D_{\text{calc}}$ ( $\text{g cm}^{-3}$ )	3.106	3.642
Absorption correction	Multi-scan	Empirical
Absorption coefficient ( $\text{mm}^{-1}$ )	7.420	9.234
$F(000)$	792	900
Crystal size (mm)	$0.300 \times 0.300 \times 0.200$	$0.150 \times 0.150 \times 0.100$
$\theta$ Range ( $^\circ$ )	3.10–27.46	3.10–25.67
Limiting indices	(–20, –8, –12) to (15, 9, 12)	(–19, –8, –11) to (19, 4, 11)
$R_{\text{int}}$	0.0409	0.0204
Reflections collected	3139	2359
Independent reflections	1001	838
Parameter/restraints/date (obs)	84/0/967	84/0/833
GOF on $F^2$	1.003	1.015
<i>Final R indices</i> [ $I > 2\sigma(I)$ ]		
$R_1$	0.0202	0.0161
$R_2$	0.0538	0.0397
<i>R indices (all data)</i>		
$R_1$	0.0208	0.0164
$R_2$	0.0539	0.0399
Largest difference peak and hole ( $e \text{\AA}^{-3}$ )	0.674 and –0.668	0.790 and –0.840

$$R_1 = \sum \|F_{\text{obs}} - |F_{\text{calc}}|\| / \sum |F_{\text{obs}}|, wR_2 = [\sum w(F_{\text{obs}}^2 - F_{\text{calc}}^2)^2 / \sum w(F_{\text{obs}}^2)]^{1/2}.$$

**Table 2**

Atomic coordinates and equivalent isotropic displacement parameters for compounds  $\text{LiM}(\text{PO}_3)_4$  ( $M = \text{Y, Dy}$ )

Atom	Site	x	y	z	$U_{\text{eq}}^a$
<i>LiY(PO<sub>3</sub>)<sub>4</sub></i>					
Li1	4e	0.5000	0.2943(8)	0.2500	0.0122(12)
Y1	4e	0.0000	0.29695(4)	0.2500	0.00499(14)
P1	8f	0.36249(4)	0.44829(8)	0.34045(7)	0.00486(16)
P2	8f	0.14647(4)	0.34979(8)	0.09709(7)	0.00483(16)
O1	8f	0.38703(14)	0.2847(2)	0.4574(2)	0.0096(4)
O2	8f	0.15711(13)	0.1258(2)	0.0795(2)	0.0084(3)
O3	8f	0.25535(12)	0.4217(2)	0.15812(19)	0.0085(3)
O4	8f	0.12780(13)	0.3840(2)	0.2296(2)	0.0094(3)
O5	8f	0.43489(12)	0.4976(2)	0.2975(2)	0.0082(3)
O6	8f	0.07078(12)	0.4159(2)	–0.08350(19)	0.0086(3)
<i>LiDy(PO<sub>3</sub>)<sub>4</sub></i>					
Li1	4e	0.50000	0.2941(14)	0.75000	0.016(2)
Dy1	4e	0.50000	0.20284(3)	0.25000	0.00537(14)
P1	8f	0.35320(7)	0.15119(14)	0.40302(12)	0.0058(2)
P2	8f	0.36231(7)	0.55240(14)	0.33977(12)	0.0055(2)
O1	8f	0.3865(2)	0.7167(4)	0.4557(4)	0.0107(6)
O2	8f	0.4288(2)	0.0859(4)	0.5831(3)	0.0094(6)
O3	8f	0.43470(19)	0.5026(4)	0.2974(3)	0.0087(5)
O4	8f	0.25537(19)	0.5786(4)	0.1575(3)	0.0090(6)
O5	8f	0.3717(2)	0.1155(4)	0.2708(3)	0.0105(6)
O6	8f	0.3427(2)	0.3748(4)	0.4192(3)	0.0094(5)

<sup>a</sup>  $U_{\text{eq}}$  is defined as one third of the trace of the orthogonalized  $U_{ij}$  tensor.

numerical integration of the Brillouin zone is performed using a  $4 \times 4 \times 3$  Monkhorst-Pack  $k$ -point sampling for it. The interactions between the ionic cores and the electrons are described by the norm-conserving pseudopotential, [16] in which the orbital electrons of  $\text{Li}-2s^1$ ,  $\text{O}-2s^2 2p^4$ ,  $\text{P}-3s^2 3p^3$ , and  $\text{Y}-4d^1 5s^2$  are treated as valence electrons.

### 3. Results and discussion

The structures of  $\text{LiM}(\text{PO}_3)_4$  ( $M = \text{Y, Dy}$ ) are isostructural and crystallize in the monoclinic system, space group  $C2/c$  (No. 15) (Table 1).

Crystal structure of  $\text{LiY}(\text{PO}_3)_4$  features a three-dimensional framework made up from 1D  $[\text{PO}_4]^{3-}$  zig-zag chains and 1D chains involving  $\text{MO}_8$  and  $\text{LiO}_4$  polyhedra, as shown in Fig. 1(a). There are two phosphorus atoms, one lithium and one yttrium atom in the asymmetric unit of  $\text{LiY}(\text{PO}_3)_4$ . The phosphorus atoms are tetrahedrally surrounded by four oxygen atoms with P–O distances ranging from 1.4832(17) to 1.6013(17) Å, and the O–P–O angles range from  $100.70(9)^\circ$  to  $119.66(11)^\circ$  (Table 1). Two neighbouring  $\text{PO}_4$  tetrahedra are interconnected via a common corner [O(2) or O(3)] to form a  $[\text{PO}_4]^{3-}$  infinite 1D zig-zag chain parallel to  $b$ -axis. Comparable to those reported in the other rare earth phosphate [17], the P–O distances for the P–O–P bridges [1.5840(18)–1.6013(17) Å] are longer than the remaining P–O bonds [1.4832(17)–1.4953(18) Å]. The lithium(I) cation is tetrahedrally coordinated by four oxygen atoms with Li–O distances 1.970(5) Å [Li(1)–O(6)  $\times$  2] and 1.980(4) Å [Li(1)–O(5)  $\times$  2], which are comparable to those reported for other lithium oxide compounds [18]. These O–Li(1)–O angles are in the range of  $82.8(2)$ – $126.0(7)^\circ$ , resulting in the largely distorted of  $\text{LiO}_4$  tetrahedra. It should be noted that there is one weak Li(1)–O(2) contacts of 2.6999 Å which has not been listed in Table 3. Y(1) is eight-coordinated by eight oxygen atoms from eight  $[\text{PO}_4]^{3-}$  anions in a square anti-prismatic geometry, with the bond length ranging from 2.2786(18) to 2.5103(18) Å. Each  $\text{YO}_8$  polyhedron is edge-connected to two  $\text{LiO}_4$  tetrahedra forming straight 1D Y–Li chains parallel to  $b$ -axis, as shown in Fig. 1(b). Y–Li straight chains and  $[\text{PO}_4]^{3-}$  wavy chains are interconnected via corner- and edge-sharing forming the 3D network of  $\text{LiY}(\text{PO}_3)_4$ .

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