# Electronic Supplementary Information

## The growth of large $GdPO_4$ crystal guided by theoretical simulation and the study of its phonon properties

Zhongmin Yang,[ac] Xinghong Gong,[a] Yujin Chen,[a] Jianhua Huang,[a] Yanfu Lin,[a] Zundu Luo,[a] Shuiquan Deng *[b] and Yidong Huang *[a]

[a]*Key Laboratory of Optoelectronic Materials Chemistry and Physics, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou, Fujian, 350002, People's Republic of China*

[b]*State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou, Fujian, 350002, People's Republic of China*

[c]*University of Chinese Academy of Sciences, Beijing, 100049, People's Republic of China*

## 1. Computational details

### 1.1. Surface energies and lattice dynamics calculation details

In this work, all the first-principle calculations were performed on the basis of the density functional theory (DFT).[1] The projector augmented wave (PAW) pseudopotentials with the *f* electrons treated as core states were applied to describe the electron-ion interactions.[2,3] The Generalized Gradient Approximation (GGA) with the Perdew-Burke-Ernzerhof functional for solids (PBEsol) was used to express the exchange-correlation potential. An energy cutoff of 520 eV and appropriate k-point meshes were chosen to ensure the convergence of the total energy in 1 meV per formula unit. The structure relaxations were performed with a force convergence criterion of 0.03 eV/Å for the surface energies calculation. The convergence precision for the lattice dynamics calculation was $1 \times 10^{-8}$ eV/Å.

### 1.2. Structural relaxation

The structure data of $GdPO_4$ was obtained from the Inorganic Crystal Structure Database with ICSD ID: 79753.[4] The experimental structural parameters were relaxed before used for all further calculations. In this work, all calculations and analyses are based on the standardized crystal structure data of $GdPO_4$, in which the relaxed lattice parameters are $a$ = 6.310 Å, $b$ = 6.823 Å, $c$ = 7.951 Å, $\alpha = \gamma$ = 90.00°, and $\beta$ = 126.15°, and in good agreement with the experimental ones.[4–7]

### 1.3. Obtaining free energy change

The free energy of a substance can be calculated by the first-principle method, and then the free energy change of a chemical reaction can be obtained by using Eq. (3) in section 2.1. The free energy for most common compounds are available in the database of the Materials Project,[8] which is built on the first-principle methods. Thus we predicted the possible chemical reaction equation according to the proportion of reactants and searched the free energy of each substance in the database to estimate the change of the free energy, $\Delta F[c;a,b]$.

## 2. Supplementary Figures

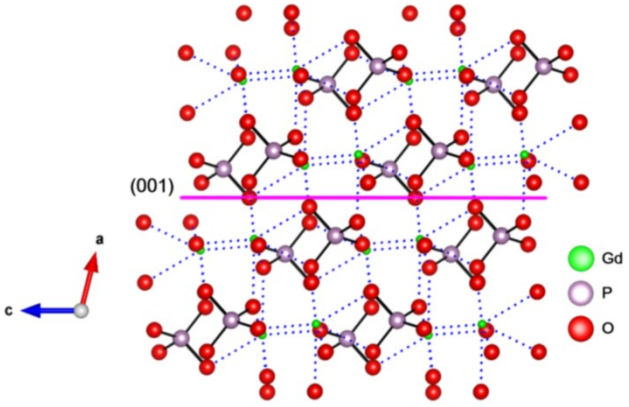


**Figure S1** The determined (001) surface (pink solid line) of $GdPO_4$ with an O atom located on the crystal plane. The blue dotted lines represent Gd-O bonds and the black solid lines are P-O bonds.

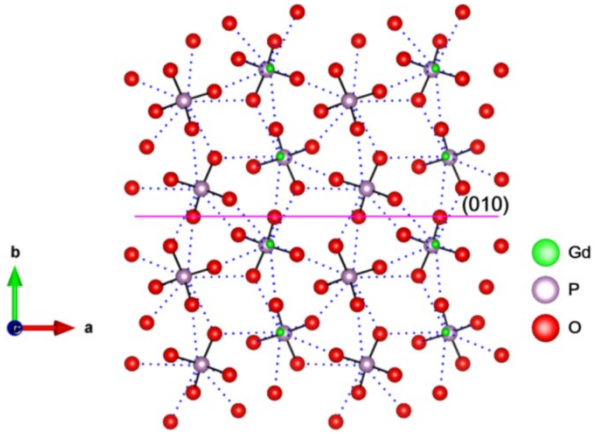


**Figure S2** The structure of the (010) surface of $GdPO_4$ with an O atom located on the crystal plane.

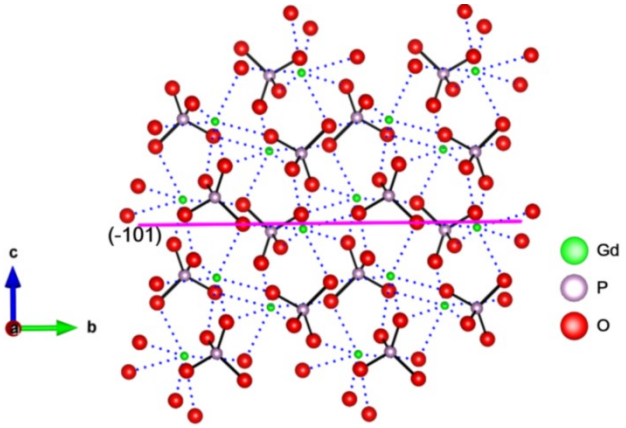


**Figure S3** The structure of the (-101) surface of $GdPO_4$ with an O atom located on the crystal plane.

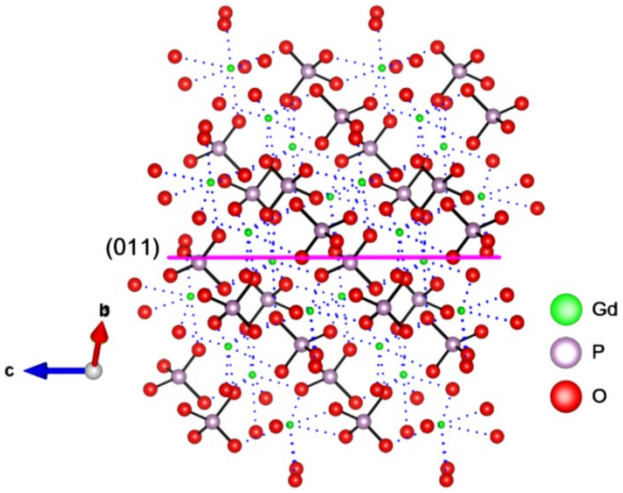


**Figure S4** The structure of the (011) surface of $GdPO_4$ with an O atom located on the crystal plane.

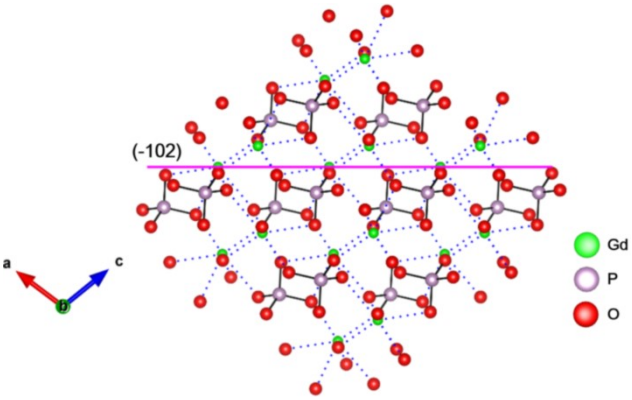


**Figure S5** The structure of the (-102) surface of $GdPO_4$ with a Gd atom located on the crystal plane.

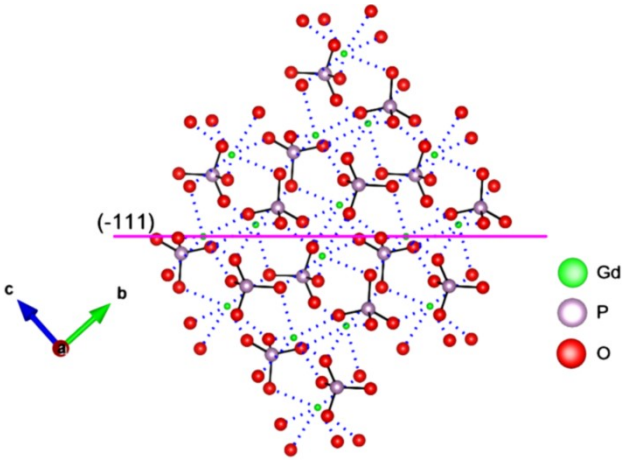


**Figure S6** The structure of the (-111) surface of $GdPO_4$ with a Gd atom located on the crystal plane.

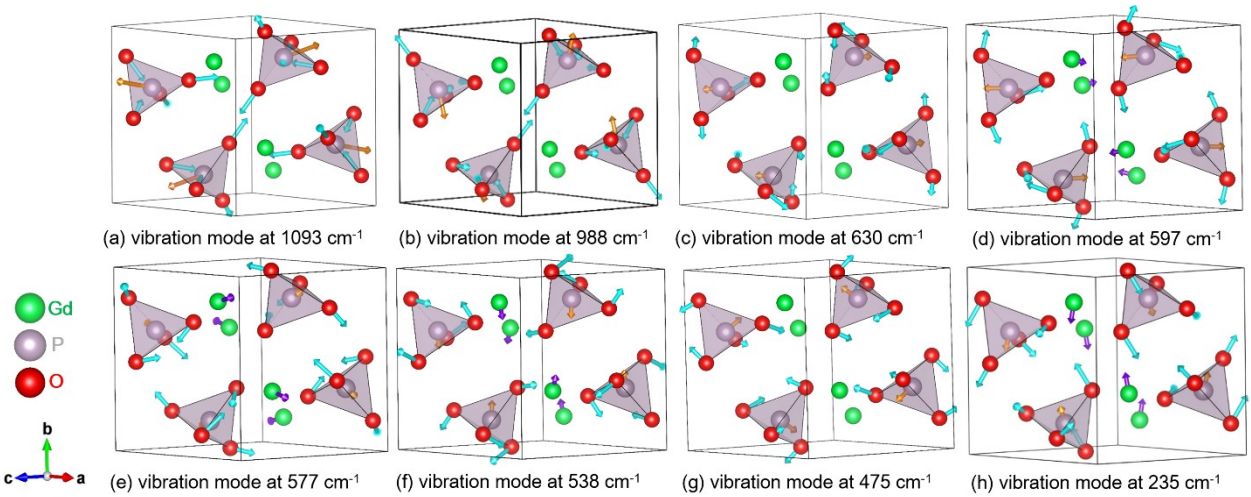


**Figure S7** Calculated atomic displacements for some modes of $GdPO_4$ with experimental frequencies in wavenumbers.

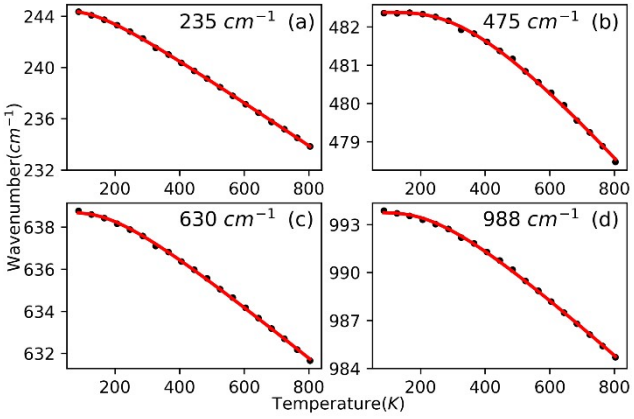


**Figure S8** Temperature-dependent Raman frequencies in wavenumbers for the selected peaks, the peaks were denoted by their peak positions according to Figure 5. (a) 235 $cm^{-1}$, (b) 475 $cm^{-1}$, (c) 630 $cm^{-1}$ and (d) 988 $cm^{-1}$. The red solid curves are fitted ones according to Eq. (5).

## 3. Supplementary Tables

**Table S1** Candidate atomic planes, each defined by a crystal plane and an atom located on it, and the number of broken Gd-O bonds a plane cuts.

| Surfaces | Atoms on the planes | Number of broken Gd-O bond |
|---|---|---|
| (001) | O (0.340,0.102,0.027) | 6 |
| | O (0.406,0.714,0.119) | 8 |
| (010) | O (0.184,0.001,0.246) | 8 |
| | O (0.119,0.165,0.616) | 8 |
| (-101) | O (0.815,0.501,0.253) | 12 |
| | O (0.660,0.898,0.973) | 8 |
| (011) | O (0.119,0.165,0.616) | 8 |
| | O (0.340,0.102,0.027) | 10 |
| | O (0.406,0.786,0.619) | 12 |
| (-111) | Gd (0.185,0.845,0.782) | 12 |
| | O (0.881,0.665,0.884) | 12 |
| | O (0.185,0.499,0.746) | 12 |
| (-102) | O (0.340,0.398,0.527) | 16 |
| | Gd (0.815,0.345,0.719) | 12 |
| (100) | O (0.881,0.835,0.384) | 8 |
| | O (0.594,0.286,0.881) | 12 |
| (-112) | O (0.815,0.501,0.254) | 14 |
| | O (0.340,0.102,0.027) | 18 |
| (110) | O (0.406,0.786,0.619) | 14 |
| | Gd (0.185,0.845,0.782) | 14 |

**Table S2** The unit cell parameters of the slab models for determining the surfaces, each unit cell contains the same number of atoms as that of the bulk $GdPO_4$.

| Surfaces | Atoms on the surfaces | *a* | *b* | *c* | *γ* |
|---|---|---|---|---|---|
| (001) | O (0.340,0.102,0.027) | 6.29 | 6.81 | 16.08 | 90.00° |
| (010) | O (0.184,0.001,0.246) | 6.29 | 6.62 | 16.81 | 104.17° |
| | O (0.119,0.165,0.616) | 6.29 | 6.62 | 18.01 | 104.17° |
| (-101) | O (0.660,0.898,0.973) | 6.62 | 6.81 | 16.92 | 90.00° |
| (011) | O (0.119,0.165,0.616) | 6.29 | 9.50 | 15.53 | 99.82° |
| (-102) | Gd (0.815,0.345,0.719) | 6.81 | 10.19 | 13.00 | 90.00° |
| (-111) | Gd (0.185,0.845,0.782) | 6.62 | 9.27 | 14.02 | 99.55° |
| | O (0.881,0.665,0.884) | 6.62 | 9.27 | 16.37 | 99.55° |
| | O (0.185,0.499,0.746) | 6.62 | 9.27 | 16.51 | 99.55° |
| (100) | O (0.881,0.835,0.384) | 6.81 | 7.94 | 13.90 | 90.00° |
| (-112) | O (0.815,0.501,0.254) | 9.27 | 9.50 | 15.59 | 114.27° |
| (110) | O (0.406,0.786,0.619) | 7.94 | 9.27 | 13.81 | 113.49° |
| | Gd (0.185,0.845,0.782) | 7.94 | 9.27 | 16.57 | 113.49° |

**Table S3** Surface energies of the $GdPO_4$ crystal.

| Surfaces | (010) | (011) | (001) | (-102) | (-101) |
|---|---|---|---|---|---|
| $E_s$ (J/m$^2$) | 0.752 | 0.707 | 0.783 | 1.143 | 1.202 |
| Surfaces | (-111) | (100) | (110) | (-112) | |
| $E_s$ (J/m$^2$) | 1.412 | 2.197 | 3.057 | 3.644 | |

**Table S4** The calculated Raman frequencies of $GdPO_4$ and the assignments for the modes.

| Modes | Calculated Raman frequency ($cm^{-1}$) |
|---|---|
| $B_g(v_3)$ | 1064 |
| $A_g(v_3)$ | 1047 |
| $B_g(v_3)$ | 1043 |
| $B_g(v_3)$ | 1012 |
| $A_g(v_3)$ | 1001 |
| $A_g(v_3)$ | 977 |
| $B_g(v_1)$ | 948 |
| $A_g(v_1)$ | 938 |
| $A_g(v_4)$ | 607 |
| $B_g(v_4)$ | 604 |
| $A_g(v_4)$ | 567 |
| $B_g(v_4)$ | 546 |
| $A_g(v_4)$ | 537 |
| $B_g(v_4)$ | 509 |
| $A_g(v_2)$ | 501 |
| $A_g(v_2)$ | 459 |
| $A_g(v_2)$ | 407 |
| $B_g(v_2)$ | 384 |
| $A_g(R)$ | 310 |
| $B_g(T)$ | 296 |
| $B_g(T)$ | 277 |
| $A_g(T)$ | 266 |
| $B_g(T)$ | 246 |
| $A_g(R)$ | 240 |
| $B_g(R)$ | 234 |
| $A_g(T)$ | 191 |
| $A_g(T)$ | 189 |
| $B_g(R)$ | 182 |
| $A_g(R)$ | 178 |
| $B_g(R)$ | 156 |
| $B_g(T)$ | 136 |
| $B_g(T)$ | 129 |
| $A_g(R)$ | 124 |
| $A_g(T)$ | 108 |
| $A_g(T)$ | 86 |
| $B_g(R)$ | 84 |

**Table S5** The values of the fitted parameters $A^{'}$, $\omega_0{}^{'}$ and $\omega^{'}$ of Eq.(5), the units of these values were given in the parentheses in the first row, respectively.

| Peaks ($cm^{-1}$) | $A^{'}$ ($cm^{-1}$) | $\omega_0{}^{'}$ ($cm^{-1}$) | $\omega^{'}$ ($cm^{-1}$) |
|---|---|---|---|
| 235 | -7.09 | 244.40 | 286.38 |
| 475 | -13.12 | 482.36 | 828.57 |
| 630 | -7.46 | 638.69 | 406.95 |
| 988 | -15.79 | 993.71 | 566.21 |

## 4. References


1 P. Hohenberg and W. Kohn, Inhomogeneous electron gas, *Phys. Rev. B*, 1964, **136**, B864.

2 P. E. Blochl, Projector augmented-wave method, *Phys. Rev. B*, 1994, **50**, 17953–17979.

3 G. Kresse and D. Joubert, From ultrasoft pseudopotentials to the projector augmented-wave method, *Phys. Rev. B*, 1999, **59**, 1758–1775.

4 Y. Ni, J. M. Hughes and A. N. Mariano, Crystal chemistry of the monazite and xenotime structures, *Am. Mineral.*, 1995, **80**, 21–26.

5 D. F. Mullica, D. A. Grossie and L. A. Boatner, Coordination geometry and structural determinations of $SmPO_4$, $EuPO_4$ and $GdPO_4$, *Inorg. Chim. Acta*, 1985, **109**, 105–110.

6 K. M. Heffernan, N. L. Ross, E. C. Spencer and L. A. Boatner, The structural response of gadolinium phosphate to pressure, *J. Solid State Chem.*, 2016, **241**, 180–186.

7 R. Lacomba-Perales, D. Errandonea, Y. Meng and M. Bettinelli, *Phys. Rev. B*, 2010, 81.

8 A. Jain, S. P. Ong, G. Hautier, W. Chen, W. D. Richards, S. Dacek, S. Cholia, D. Gunter, D. Skinner, G. Ceder and K. A. Persson, Commentary: The Materials Project: A materials genome approach to accelerating materials innovation, *APL Mater.*, 2013, **1**, 011002.