Synthesis, crystal and electronic structure, and physical properties of a

new quaternary phosphide Ba<sub>4</sub>Mg<sub>2+ $\delta$ </sub>Cu<sub>12- $\delta$ </sub>P<sub>10</sub> (0 <  $\delta$  < 2)

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## **Supporting information**

- 1. **Figure S1.** Calculated and experimental powder X-ray diffraction patterns for Ba4Mg2.8Cu<sub>11.2</sub>P<sub>10</sub>.
- 2. **Figure S2.** Calculated and experimental powder X-ray diffraction patterns for Ba<sub>4</sub>Mg<sub>2+ $\delta$ </sub>Cu<sub>12- $\delta$ </sub>P<sub>10</sub> ( $\delta$  = 0, 0.8, 1.0, 1.5, 2.0, 2.5) samples.
- 3. **Figure S3.** An enlarged view of the fragments of powder X-ray diffraction patterns for  $Ba_4Mg_{2+\delta}Cu_{12-\delta}P_{10}$  around  $2\theta = 34.5^{\circ}$ .
- 4. **Figure S4.** The unit cell volume *vs.* nominal composition plot for  $Ba_4Mg_{2+\delta}Cu_{12-\delta}P_{10}$ .
- 5. **Table S1.** EDS results of  $Ba_4Mg_{2+\delta}Cu_{12-\delta}P_{10}$ .
- 6. **Figure S5.** SEM image of the  $Ba_4Mg_{2.8}Cu_{11.2}P_{10}$  crystal.



Figure S1. Calculated and experimental powder X-ray diffraction patterns for Ba<sub>4</sub>Mg<sub>2.8</sub>Cu<sub>11.2</sub>P<sub>10</sub>.



**Figure S2.** Calculated and experimental powder X-ray diffraction patterns for Ba<sub>4</sub>Mg<sub>2+ $\delta$ </sub>Cu<sub>12- $\delta$ </sub> P<sub>10</sub> ( $\delta$  = 0, 0.8, 1.0, 1.5, 2.0, 2.5) samples. Red squares indicate the main admixture peak.



**Figure S3.** An enlarged view of the fragments of calculated and experimental powder X-ray diffraction patterns for Ba<sub>4</sub>Mg<sub>2+ $\delta$ </sub>Cu<sub>12- $\delta$ </sub>P<sub>10</sub> ( $\delta$  = 0, 0.8, 1.0, 1.5, 2.0, 2.5) around 2 $\theta$  = 34.5°.



**Figure S4.** The unit cell volume *vs.* nominal composition plot for  $Ba_4Mg_{2+\delta}Cu_{12-\delta}P_{10}$ . The powder X-ray diffraction data collected at room temperature are shown as orange diamonds. A volume of the single crystal studied at 90 K is shown as blue star.



**Table S1.** Results of EDS analyses of selected single crystals of  $Ba_4Mg_{2+\delta}Cu_{12-\delta}P_{10}$ .



Figure S5. An SEM image of the Ba4Mg2.8Cu11.2P10 crystal.