## **Supporting Information**

## **Piezochromism and Anomalous Near-Infrared Luminescence Evolution of BaCuSi<sub>4</sub>O<sub>10</sub> and BaCuSi<sub>2</sub>O<sub>6</sub> via Pressure-Induced Phase Transition**

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**Figure S1.** Rietveld refinement results of BaCuSi<sub>4</sub>O<sub>10</sub> powder XRD patterns at ambient condition.

Figure S2. Rietveld refinement results of BaCuSi<sub>2</sub>O<sub>6</sub> powder XRD patterns at ambient condition.

Figure S3. NIR emission spectra of  $BaCuSi_4O_{10}$  and  $BaCuSi_2O_6$  at ambient condition.

Figure S4. The decay time of BaCuSi<sub>4</sub>O<sub>10</sub> and BaCuSi<sub>2</sub>O<sub>6</sub> at ambient condition.

Figure S5. NIR emission spectra of  $BaCuSi_4O_{10}$  at 0.3 GPa and after pressure release.

Figure S6. NIR emission spectra of  $BaCuSi_2O_6$  at 0.4 GPa and after pressure release.

Figure S7. LeBail fitting results of  $BaCuSi_4O_{10}$  at (a) 0.2 GPa, (b) 3.1 GPa, and (c) 17.3 GPa.

Figure S8. XRD patterns of BaCuSi<sub>4</sub>O<sub>10</sub> at 0.2 GPa and after pressure release.

Figure S9. The Raman spectra of BaCuSi<sub>4</sub>O<sub>10</sub> at 0.4 GPa and after pressure release.

Figure S10. LeBail fitting results of BaCuSi<sub>2</sub>O<sub>6</sub> at (a) 0.2 GPa, (b) 14.7 GPa.

Figure S11. (a) In situ HP cell parameters of BaCuSi<sub>2</sub>O<sub>6</sub> under selected pressure, and (b)

the cell volume as a function of applied pressure.

Figure S12. *in situ* HP Raman spectra of BaCuSi<sub>2</sub>O<sub>6</sub>.

Figure S13. XRD patterns of BaCuSi<sub>2</sub>O<sub>6</sub> at 0.2 GPa and after pressure release.

Figure S14. The Raman spectra of  $BaCuSi_2O_6$  at 0.3 GPa and after pressure release.

Figure S15. Optical photos of BaCuSi<sub>2</sub>O<sub>6</sub> during compression.



Figure S1. Rietveld refinement results of  $BaCuSi_4O_{10}$  powder XRD patterns at ambient condition.



Figure S2. Rietveld refinement results of  $BaCuSi_2O_6$  powder XRD patterns at ambient condition.



Figure S3. NIR emission spectra of  $BaCuSi_4O_{10}$  and  $BaCuSi_2O_6$  at ambient condition.



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Figure S5. NIR emission spectra of BaCuSi<sub>4</sub>O<sub>10</sub> at 0.3 GPa and after pressure release.



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Figure S8. XRD patterns of  $BaCuSi_4O_{10}$  at 0.2 GPa and after pressure release.



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