## **Electronic Supplementary Information (ESI)**

- Figure S1. TG/DTA analysis for polycrystalline K<sub>3</sub>V<sub>5</sub>O<sub>14</sub>.
- Figure S2. XRD data of residue after TG/DTA measurement.
- Figure S3. X-ray diffraction for {10-10} planes.
- Figure S4. X-ray diffraction for {0001} planes.
- Figure S5. UV-vis diffuse reflectance spectra for ground  $K_3V_5O_{14}$  crystal.
- Figure S6. Displacement versus electric field (300 V) plot for Z-cut of K<sub>3</sub>V<sub>5</sub>O<sub>14</sub> single crystal.
- Figure S7. Displacement versus electric field (500 V) plot for Z-cut of K<sub>3</sub>V<sub>5</sub>O<sub>14</sub> single crystal.
- Figure S8. Displacement versus electric field (800 V) plot for Z-cut of K<sub>3</sub>V<sub>5</sub>O<sub>14</sub> single crystal.
- Figure S9. Polarization vs. temperature data, and the temperature dependence of the pyroelectric coefficient for Z-cut of K<sub>3</sub>V<sub>5</sub>O<sub>14</sub> single crystal.
- Figure S10. Polarization vs electric field plots at 16 kV/cm at different frequencies for a Z-cut  $K_3V_5O_{14}$  single crystal.



Figure S1. TG/DTA analysis for polycrystalline K<sub>3</sub>V<sub>5</sub>O<sub>14</sub>.

Figure S2. XRD data of residue after TG/DTA measurement.







Figure S4. X-ray diffraction for {0001} planes.







Figure S6. Displacement versus electric field (300 V) plot for Z-cut of K<sub>3</sub>V<sub>5</sub>O<sub>14</sub> single crystal.



Figure S7. Displacement versus electric field (500 V) plot for Z-cut of K<sub>3</sub>V<sub>5</sub>O<sub>14</sub> single crystal.



Figure S8. Displacement versus electric field (800 V) plot for Z-cut of K<sub>3</sub>V<sub>5</sub>O<sub>14</sub> single crystal.



Figure S9. Polarization vs. temperature data (black color), and the temperature dependence of the pyroelectric coefficient (blue color) for Z-cut of  $K_3V_5O_{14}$  single crystal.



Figure S10. Polarization vs electric field plots at 16 kV/cm at different frequencies for a Z-cut  $K_3V_5O_{14}$  single crystal.

