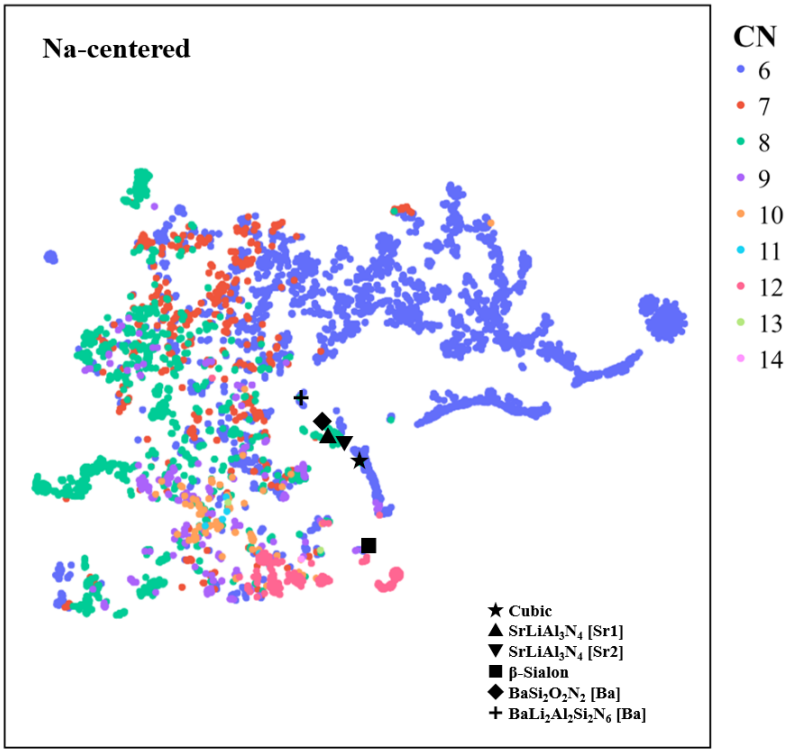


Figure S1. 2D t-SNE plot of the Na-centered local structures.

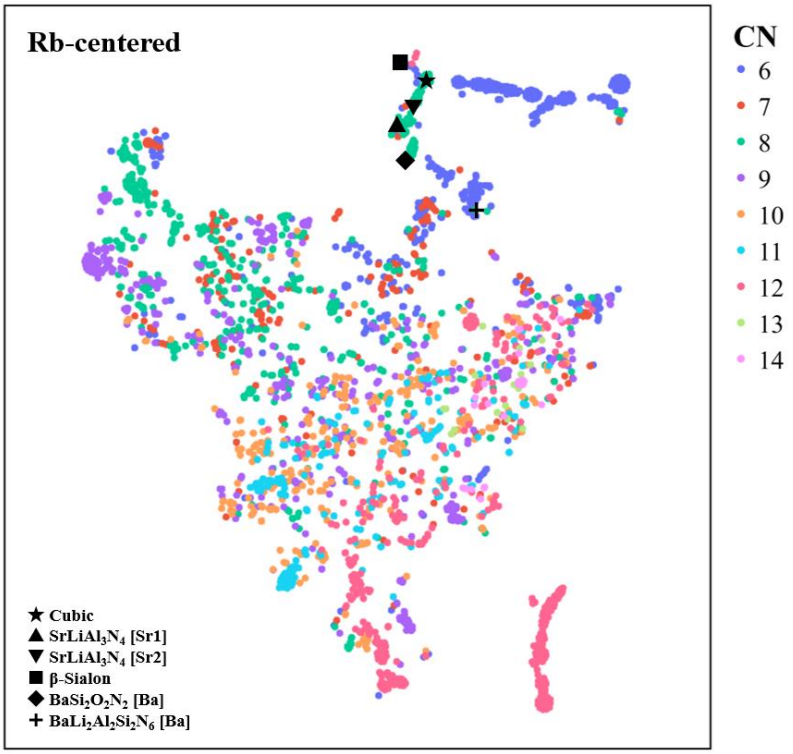


Figure S2. 2D t-SNE plot of the Rb-centered local structures.

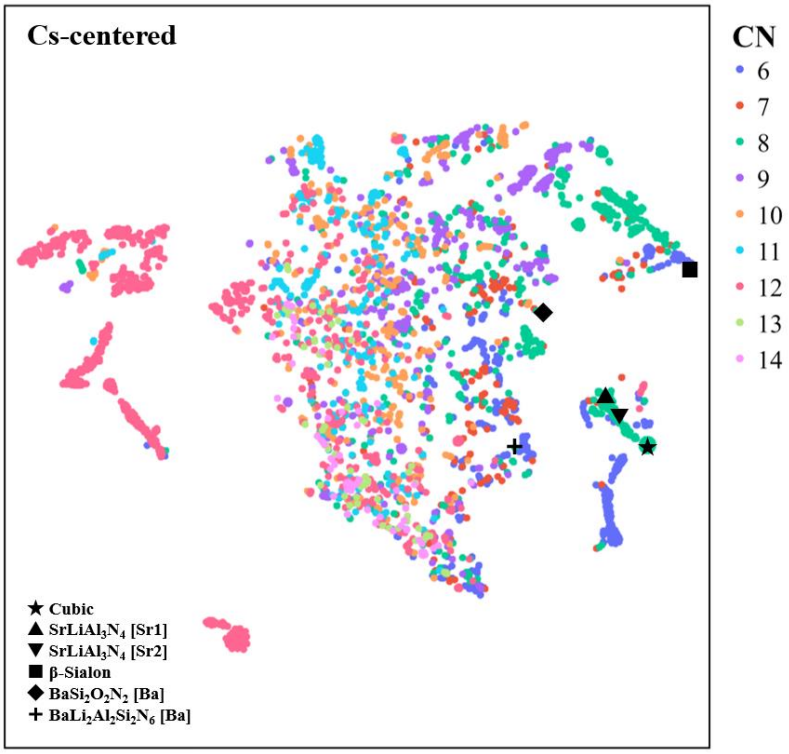


Figure S3. 2D t-SNE plot of the Cs-centered local structures.

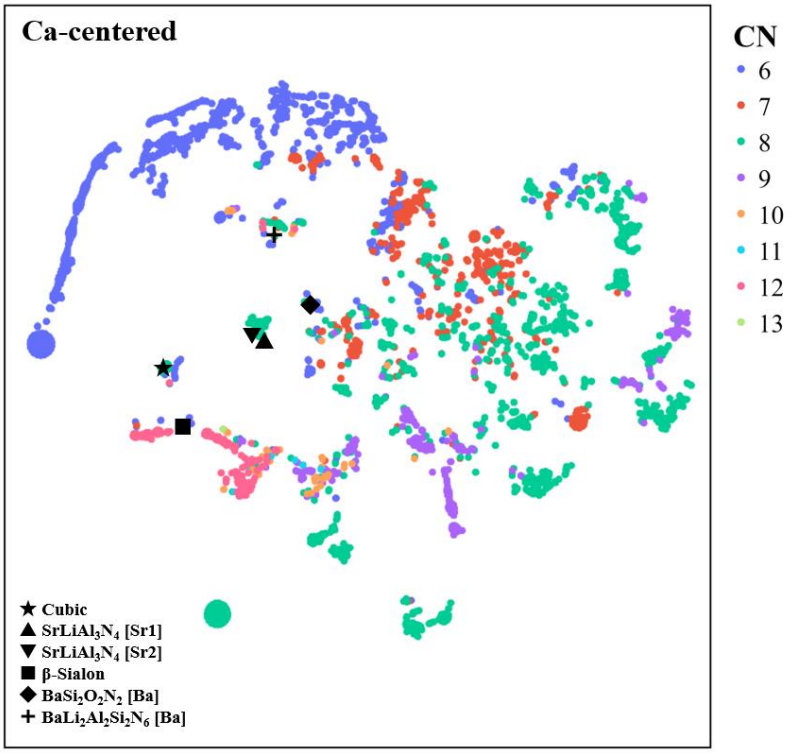


Figure S4. 2D t-SNE plot of the Ca-centered local structures.

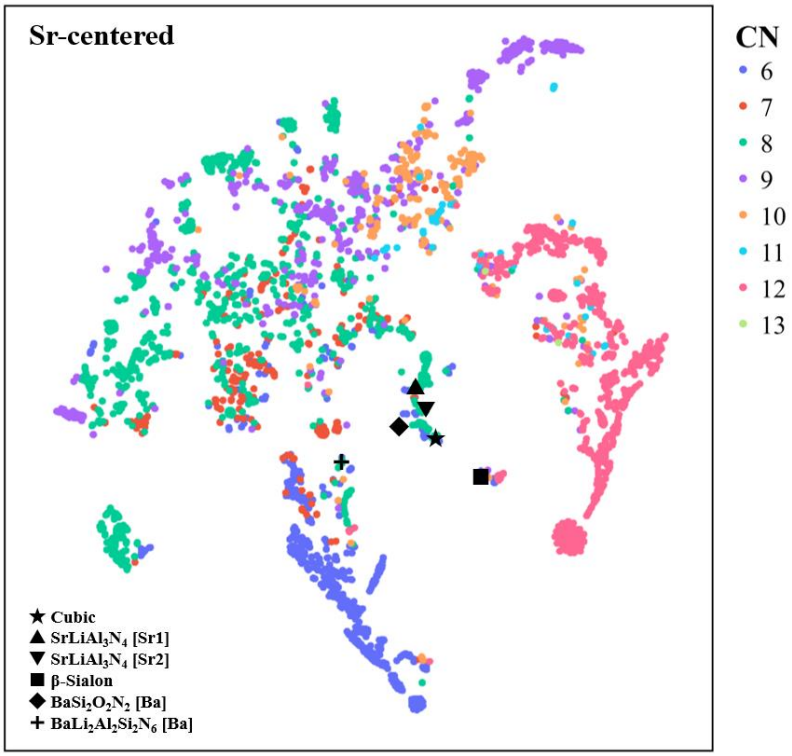


Figure S5. 2D t-SNE plot of the Sr-centered local structures.

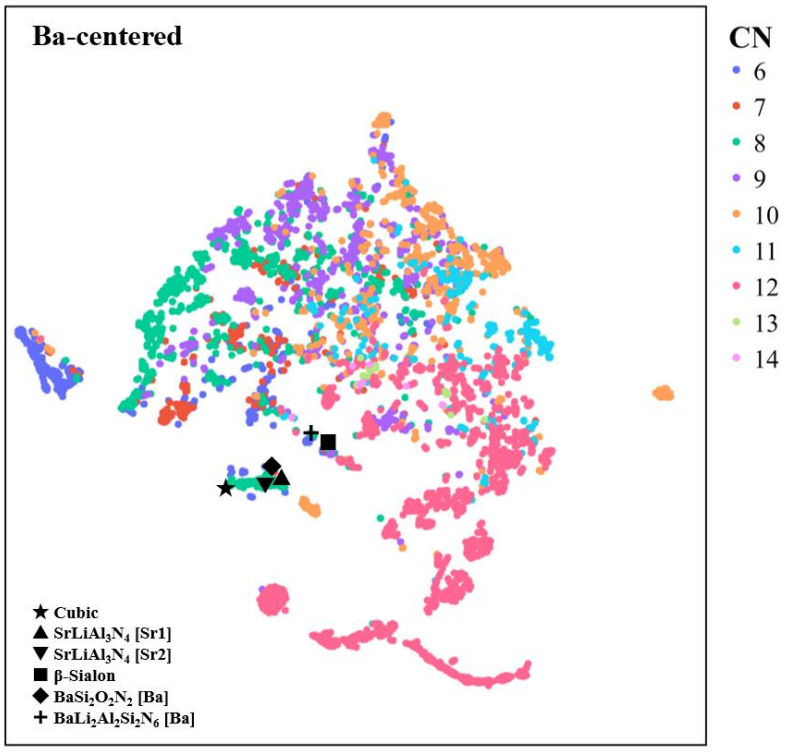


Figure S6. 2D t-SNE plot of the Ba-centered local structures.

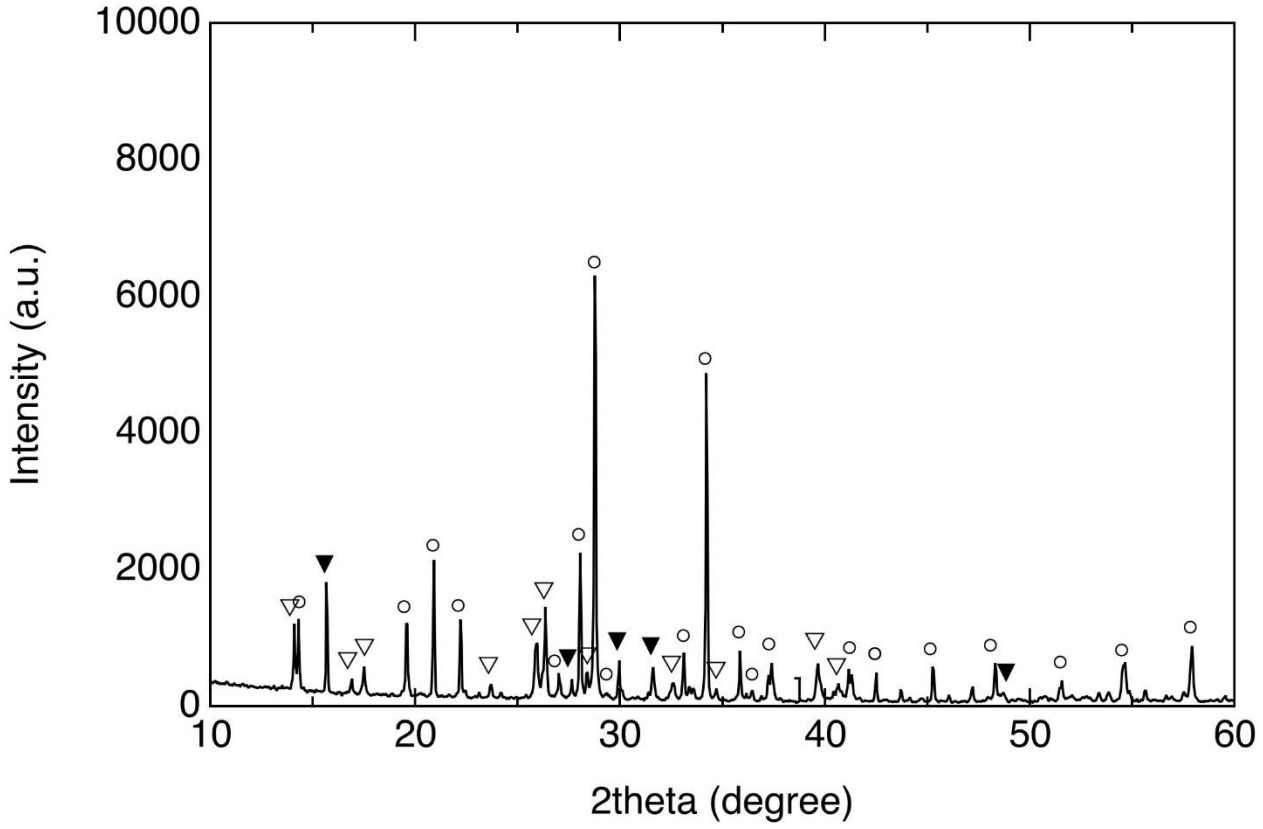


Figure S7. Powder XRD patterns of the fired product. Filled black triangles, white triangles and white circles indicate diffraction peaks from $K_2ZnP_2O_7$, $KPO_3$ and α-$KZnPO_4$, respectively.

Table S1. Atomic coordinates, occupancies, and isotropic atomic displacement parameters of $K_2ZnP_2O_7:Eu^{2+}$

| Atom | x | y | z | Ueq (Å$^2$) | Occupancy |
|---|---|---|---|---|---|
| K1 | 0.35039(7) | 0.35039(7) | 0 | 0.01568(11) | 1 |
| K2 | 0.81470(7) | 0.18530(7) | 0 | 0.01615(12) | 1 |
| Zn1 | 0.5 | 0 | 0.25 | 0.01003(6) | 1 |
| P1 | 0.13656(5) | 0.13656(5) | 0.21683(5) | 0.00807(8) | 1 |
| O1 | 0 | 0 | 0.1668(2) | 0.0131(4) | 1 |
| O2 | 0.30305(14) | 0.07872(16) | 0.15880(10) | 0.01299(18) | 1 |
| O3 | 0.13633(16) | 0.13633(16) | 0.34854(15) | 0.0151(3) | 1 |

Table S2. Crystallographic data of $K_2ZnP_2O_7:Eu^{2+}$

| | |
|---|---|
| Formula mass (g mol$^{-1}$) | 317.51 |
| Crystal system | tetragonal |
| Space group | $P4_2/mnm$ (No. 136) |
| Temperature (K) | 301(2) |
| Cell parameters (Å) | $a = b$ = 7.84328(13), $c$ = 11.3195(3) |
| Cell volume (Å$^3$) | 696.34(3) |
| $Z$ | 4 |
| Radiation type | Mo $K\alpha$ |
| $\mu$ (mm$^{-1}$) | 5.17 |
| Crystal size (mm$^3$) | 0.031 × 0.015× 0.011 |
| Diffractometer | ROD, Synergy Custom system, HyPix-Arc 150 |
| $T_{min}$, $T_{max}$ | 0.911, 0.945 |
| $R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$ | 0.0494, 0.0787 |
| $S$ | 1.457 |
| $\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å$^{-3}$) | 0.757, -0.858 |