Supporting Information

Alkali metal impact on structural and phonon properties of Er\(^{3+}\) and Tm\(^{3+}\) co-doped MY(WO\(_4\))\(_2\) (M = Li, Na, K) nanocrystals

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Figure S1. The selected diffraction patterns of (a) LiY(WO$_4$)$_2$:Er,Tm, (b) NaY(WO$_4$)$_2$:Er,Tm and (c) KY(WO$_4$)$_2$:Er,Tm nanopowders obtained by the Pechini method calcined at various temperatures (solid line) and by the hydrothermal method (broken line). Diffraction pattern of the standard monoclinic [E. Gallucci, C. Goutaudier, M.T. Cohen-Addad, B.F. Mentzen, T. Hansen, J. Alloys Compd. 306 (2000) 227] and tetragonal [Y. He, G. Wang, Z. Luo, Chin. Phys. Lett. 10 (1993) 667] phases are added for comparison.

Figure S2. Final Rietveld plot for the sample of LiY(WO$_4$)$_2$:Er,Tm calcined at 600°C. The circles are the experimental values; the continuous lines stand for the calculated pattern. Vertical bars correspond to the position of Bragg peaks of tetragonal structure (upper line), monoclinic
phase (middle line) of LiY(WO₄)₂ and of Li₂WO₄ (bottom line). The bottom curve represents the difference between experimental and calculated diffraction patterns.
**Figure S3** Lattice parameters vs. calcination temperature for (a) monoclinic and (b) tetragonal phase.

![Graph showing lattice parameters vs. calcination temperature](image)

**Figure S4.** Lattice parameter c of Li$_2$WO$_4$ nanocrystals vs calcination temperature.

![Graph showing lattice parameter c](image)
**Figure S5.** Histograms of particle size distribution of (a) LiY(WO$_4$)$_2$:Er,Tm, (b) NaY(WO$_4$)$_2$:Er,Tm and (c) KY(WO$_4$)$_2$:Er,Tm nanopowders. The fitting curves represent double-peak LogNormal approximation.

**Figure S6.** Lattice parameters of the main phase of KY(WO$_4$)$_2$:Er,Tm nanocrystals (from Pechini synthesis) vs. calcination temperature.
| Li    | Na    | K    | Assignment |
|-------|-------|------|------------|
| 600 C | 650 C | 700 C | 750 C | 850 C | 600ºC | 700ºC | 750ºC | 850ºC | unidentified |
| 942sh | 948sh | 946sh | 947sh | 927w | 949m | 927w | 927m | 926m | ν(W-O) |
| 921m | 921m | 919m | 918m | 925sh | 932w | 933w | 931w | 931w | 932w | ν(W-O) |
| 901m | 892sh | 892m | 891s | 888vs | 851sh | 858sh | 845s | 847s | 849vs | ν(W-O) |
| 833vs,b | 830vs,b | 836vs,b | 827s | 829vs,b | 790vs | 789vs | 799s | 797s | 801vs | ν(W-O) |
| 761m,b | 770m,b | 760sh | 797sh | 716s | 720m | 719m | 722m | 721m | 721m | ν(W-O) |
| 709m | 711m | 709s | 708vs | 716s | 720m | 719m | 722m | 721m | 721m | ν(W-O) |
| 616vs,b | 599s,b | 602s,b | 599vs,b | 610m | 485m | 484m | 484m | 484m | 484m | ν(W-O) |
| 532w | 531w | 525m | 515m | 483sh | 445m | 444m | 443m | 443m | 443m | δ(W-O) |
| 480m | 484m | 489m | 497sh | 487sh | 413w | 452w | 452w | 451w | 451w | δ(WOOW) |
| 391w | 394sh | 391sh | 326s,b | 328s,b | 330m,b | 332m,b | 329m,b | 328m,b | 328m,b | δ(WOOW) |
| 348m,b | 346s,b | 345s,b | 350s,b | 332w | 332w | 317m | 317m | 317m | 317m | δ(WOOW) |
| 303m | 305s | 307s | 301m | 291s,b | 289m,b | 290m,b | 290m,b | 290m,b | 285m,b | δ(WOOW) |
| 266sh | 267sh | 266sh | 208s,b | 197w | 197w | 197w | 197w | 194w | 202w | δ(WOOW) |
| 250w | 252m | 252m | 249m | 208m,b | 197w | 197w | 197w | 194w | 202w | δ(WOOW) |
| 231sh | 200m | 200w | 197w | 197w | 197w | 197w | 194w | 202w | 169m | T'(M^+/Ln3+) |
| 197w | 155w | 158w | 154w | 151w | 156m | 156m | 155m | 155m | 155m | lattice modes |
| 122w | 128w | 128w | 116s | 116w | 118w | 118w | 119w | 119w | 119w | lattice modes |

(abbreviations: vs – very strong, s – strong, m – medium, w – weak, vw – very weak, sh – shoulder, b – broad)