

Highly Efficient NIR to NIR Upconversion in ZnMoO₄:Tm³⁺,Yb³⁺,K⁺ Phosphor and in-vivo imaging

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Electronic Supplementary Information (ESI):

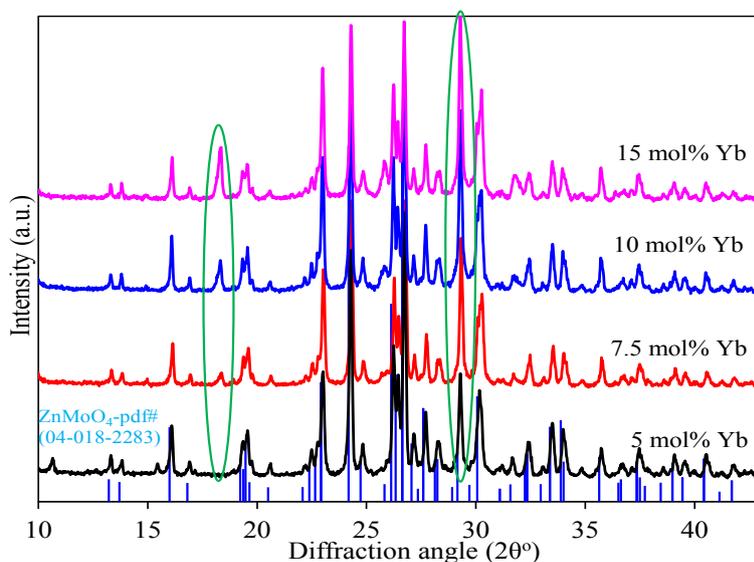


Fig. S1 XRD patterns of ZnMoO₄:0.1 mol% Tm³⁺ phosphors co-doped with different mol% of Yb³⁺.

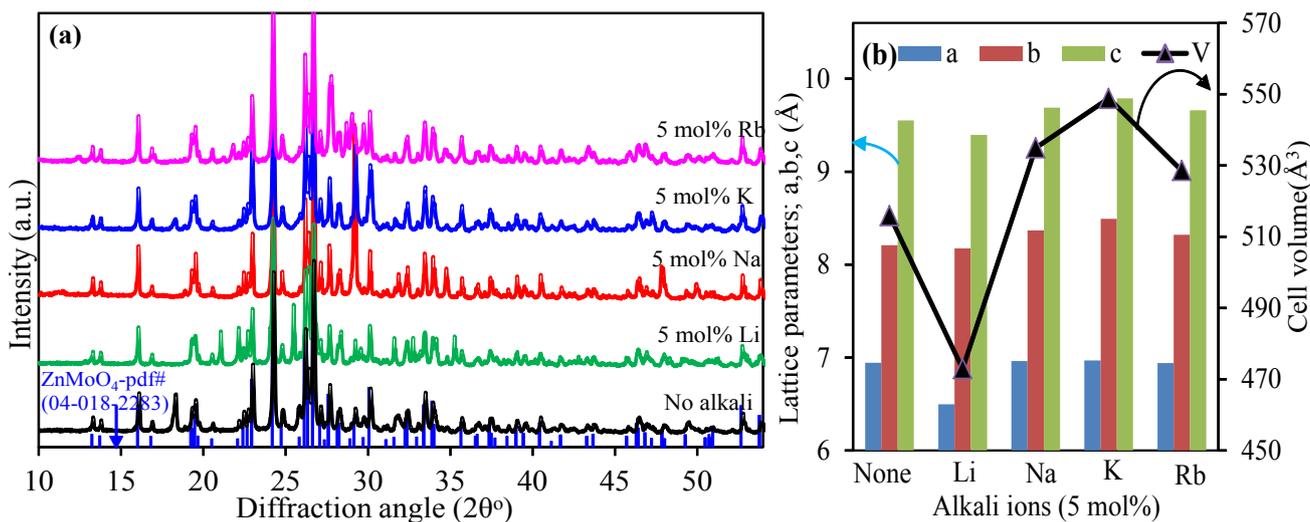


Fig. S2 (a) XRD patterns of ZnMoO₄:0.1 mol% Tm³⁺, 6 mol% Yb³⁺ phosphors co-doped with different alkali metal ions as charge compensator and (b) lattice constants (a, b,c) and unit cell volume (V) variation with the alkali metal ions substitution. It is assumed that two Zn²⁺ ions were occupied by one RE³⁺ ion and a monovalent alkali ion (A⁺) in the substituted ZnMoO₄ host to neutralize the charge as expressed as follows: 1Zn²⁺ + 1Zn²⁺ = 1RE³⁺ + 1 A⁺

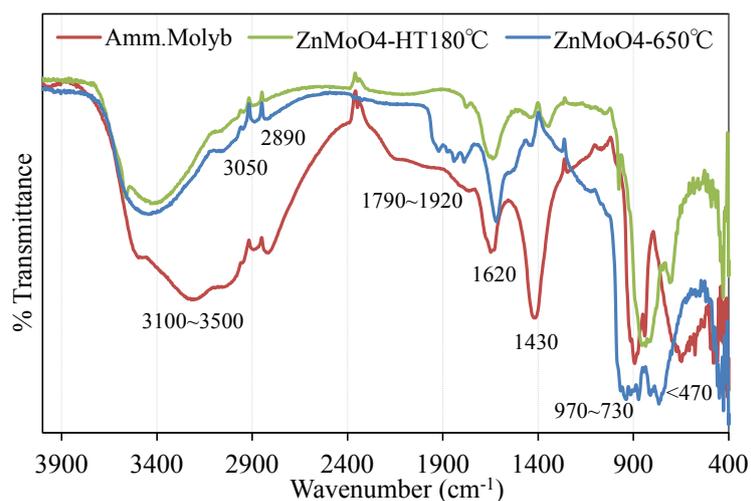


Fig. S3 FT-IR spectra of Ammonium molybdate tetrahydrate (precursor used during HT process), ZnMoO_4 phosphor prepared by HT at 180°C and ZnMoO_4 phosphor post annealed at 650°C for 1 hour.

The broad bands around 3450 cm^{-1} and 1618 cm^{-1} were assigned to the O-H stretching and H-O-H bending vibrations of the water molecules from the $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$ molecules.¹ Strong absorption bands around $730 - 970\text{ cm}^{-1}$ are related to the O-Mo-O stretches of the MoO_4 tetrahedron. The absorption bands centered around 911 cm^{-1} , 780 cm^{-1} and 430 cm^{-1} are the ν_1 , ν_3 and ν_2 modes of the MoO_4 groups.^{2,3} XRD patterns and IR peaks clearly suggest that the hydrothermally treated samples are pure ZnMoO_4 and do not contain any polymeric molybdate precursors used during the synthesis of ZnMoO_4 phosphors.

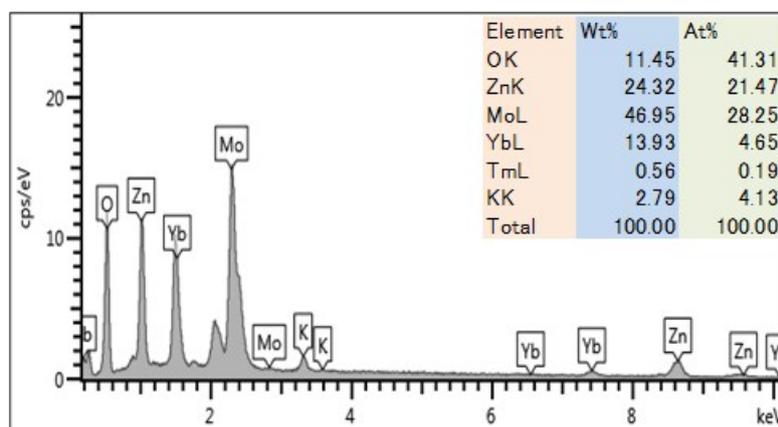


Fig. S4 Typical EDS spectrum of $\text{ZnMoO}_4:\text{Tm}^{3+}, \text{Yb}^{3+}, \text{K}^+$ sample (0.1 mm area) taken from the SEM-EDS instrument.

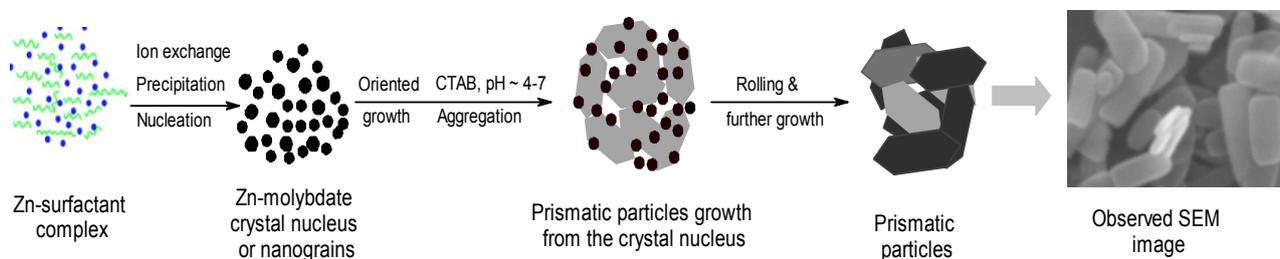


Fig. S5 Formation mechanism of prismatic $\text{ZnMoO}_4:\text{Tm}^{3+}, \text{Yb}^{3+}$ particles during hydrothermal treatment process.^{4,5}

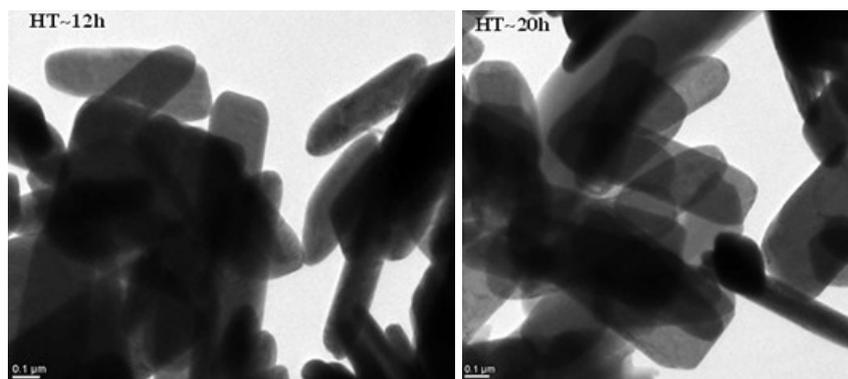


Fig. S6 TEM images of $\text{ZnMoO}_4:\text{Tm}^{3+}, \text{Yb}^{3+}$ prismatic particles growth with hydrothermal treatment time.

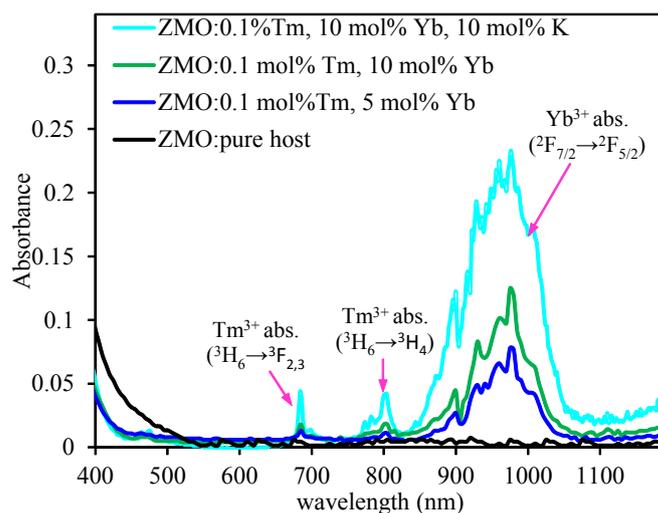


Fig. S7 Absorption spectra of $\text{ZnMoO}_4:\text{Tm}^{3+}$ phosphors with and without co-doping Yb^{3+} and K^{+} ions.

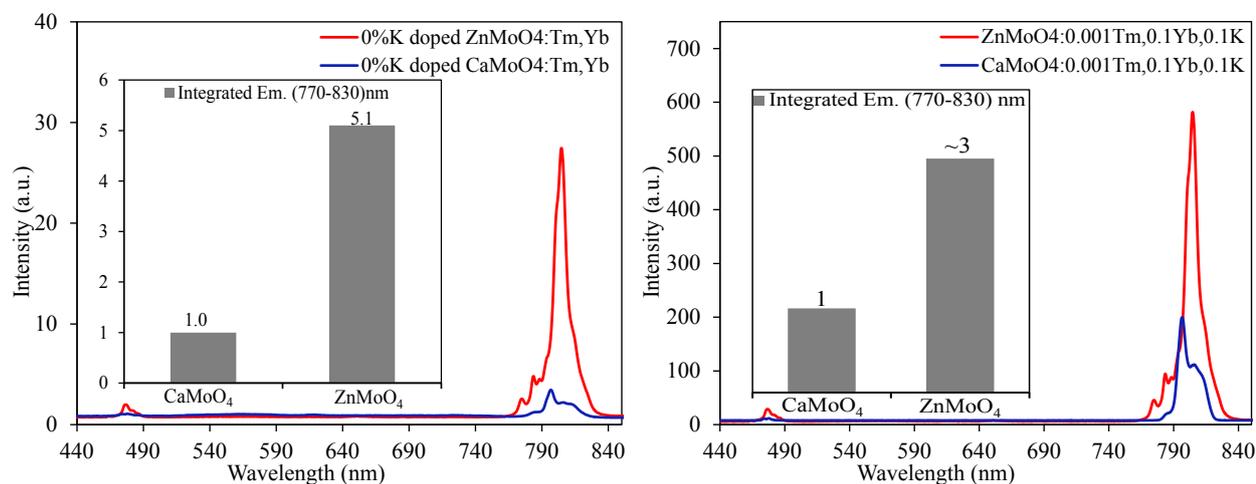


Fig. S8 Comparison of UC intensities of the $\text{ZnMoO}_4:\text{Tm}^{3+}, \text{Yb}^{3+}$ with the $\text{CaMoO}_4:\text{Tm}^{3+}, \text{Yb}^{3+}$ phosphors before (left) and after (right) optimization with 10 mol% K^{+} ions substitution. Insets are the integrated NIR emissions from 770 to 800 nm.⁶

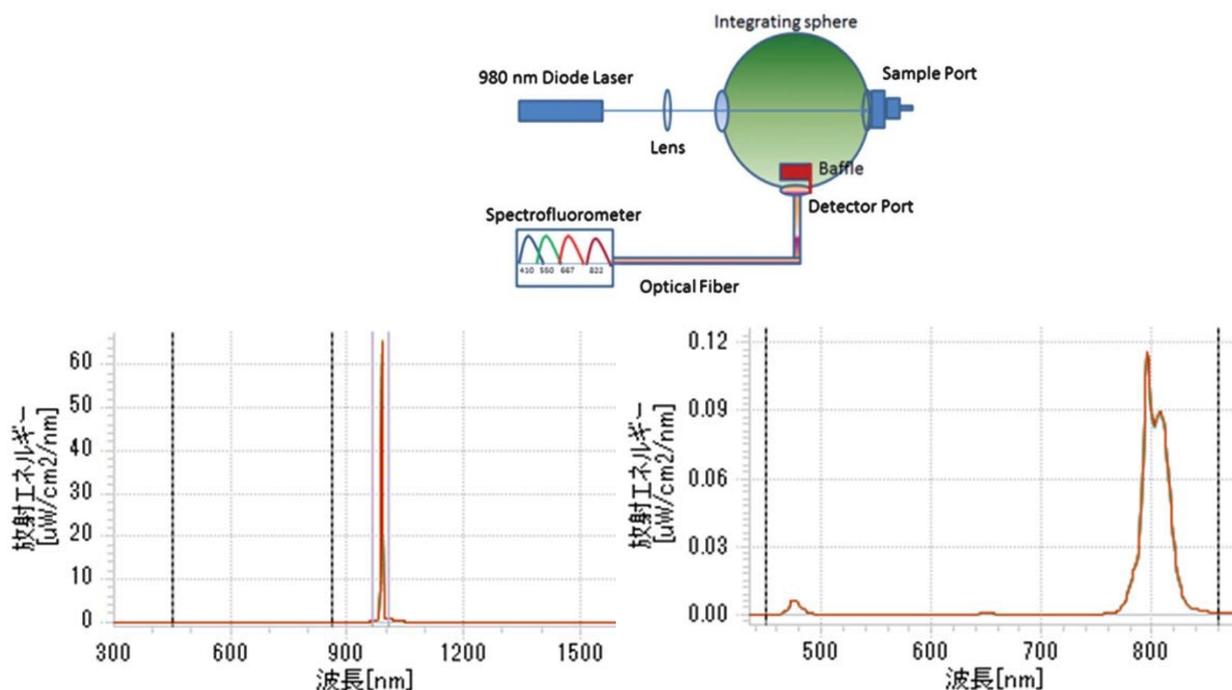


Fig. S9 Absolute quantum yield determination of the $\text{ZnMoO}_4:0.1 \text{ mol\% Tm}^{3+}, 10 \text{ mol\% Yb}^{3+}, 10 \text{ mol\% K}^+$ phosphor excited by 985 nm (50 nm bandpass filter) laser and collected emitted photons of 400-850 nm. Right figure is the enlarged portion of the emitted photon collection area. The absolute quantum yield was estimated $\sim 1.45\%$. However, small fraction of emitted photons at the visible range were included that contributed less than 0.02%.



Fig. S10 Colloidal solution of as prepared $\text{ZnMoO}_4:0.1 \text{ mol\% Tm}^{3+}, 10 \text{ mol\% Yb}^{3+}, 10 \text{ mol\% K}^+$ phosphor particles in the PBS solution (1mg/ml) and photograph of blue light emission of colloidal particles exposed to 10 mW 980 nm laser light. Since, the sample exhibit both blue and NIR@800nm lights, it is easy to visualize blue color. However, blue emission was detected only upto few mm depth.

References

1. V. C. Farmer and M. Society, *The infrared spectra of minerals*, Mineralogical Society, London, 1974.
2. S.P.S. Porto and J. F. Scott, *Phys. Rev.*, 1967, **157**, 716–719.
3. F. Lei and B. Yan, *J. Solid State Chemistry*, 2008, **181**, 855-862.
4. A. M. Kaczmarek and R. V. Deun, *Chem. Soc. Rev.*, 2013, **42**, 8835-8848
5. W. Shi, S. Song and H. Zhang, *Chem. Soc. Rev.*, 2013, **42**, 5714-5743.
6. H. N. Luitel, R. Chand, T. Torikai, M. Yada and T. Watari, *RSC Advances*, 2015, **5**, 17034-17040.