Perovskite $KMnF_3$ Nanocubes: Cationic Commingling for Technological Relevance

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Required materials

Potassium Acetate ($CH_3.COOK$)(99%, AR/ACS, Loba Chemie), Manganese(II) acetate tetrahydrate $(CH_3COO)_2Mn.4H_2O$ Pure (CDH), Cobalt Acetate Tetrahydrate $(CH_3COO)_2Co.4H_2O$, 99-102%, Loba Chemie), Erbium Nitrate Pentahydrate $Er(NO_3)_3.5H_2O$(99.9%, Alfa Aesar), Ytterbium Nitrate Pentahydrate $Yb(NO_3)_3.5H_2O$(99.9%, Alfa Aesar), 1-butyl-3-methyl tetrafluoroborate $[C_4mim]$ BF_4 ionic liquid, Ethanol (99.9%), Methanol(99.5%, Loba Chemie), Acetone (99%, Loba Chemie), De ionised (DI) Water. All these chemicals were used without further purification.

Synthesis of Ionic Liquids:

1-butyl-3-methylimidazolium bromide $[C_4mim]$ Br

First 39.2 mL 1-bromo-butane (HIMEDIA) was taken in round bottom flask and 23 mL 1-methylimidazole (Alfa Aesar) was added dropwise at continuous stirring over 30 minutes at 0°C. Then the flask was covered with aluminium foil and the reaction continues at room temperature (RT) for 4 days. The product was washed with ethyl acetate and dried in a vacuum followed by recrystallization with acetonitrile and was freezed overnight. [1]

Synthesis of 1-butyl-3-methylimidazolium tetrafluoroborate $[C_4mim]BF_4$ IL

Task specific and room temperature ionic liquid (RTIL), $[C_4mim]BF_4$ was synthesized by reacting $NaBF_4$ (21 gm) with 1-butyl-3-methylimidazolium bromide $[C_4mim]$ Br (42 gm) in

acetone (100 mL) under stirring at RT for 3-4 days. The mixture was then filtered, stirred with 1 gm activated charcoal for 16 hours. The activated charcoal was filtered and acetone was removed using a rotary evaporator under vacuum. The product was washed with dichloromethane (at least 3-4 times) to remove impurities, A little amount of silver nitrate solution was added to the washed IL to confirm the absence of chloride ions. The pale yellowish liquid was isolated and further dried under vacuum for 12 hours. [2]

Characterization techniques:

For crystal phase identification, PXRD (Powder X-ray diffraction) studies were performed using a D8 Advance BRUKER diffractometer equipped with Cu K_α (λ =0.1540 nm) in the 2θ range of 10° - 80°. The morphologies and fracture surfaces of the Ln^{3+}- doped $KZnF_3$ nanoparticles (NPs) were investigated using transmission electron microscopy (TEM) and Scanning Electron Microscopy (SEM). TEM images of the as-prepared samples were obtained with a JEOL JEM-F200 operating at 20 kV~200 kV, where the samples were dispersed on carbon-coated copper grids for conventional TEM and HRTEM imaging. Morphological characterization was also performed using FESEM (NOVA NANO SEM-450, FEI). Up conversion luminescence of as prepared samples was measured by exciting them with a 980 nm NIR laser and using a Horiba Jobin Yvon Fluoromax-4 spectrofluorometer. Magnetic properties were studied using Vibrating Sample Magnetometer ADE – EV9, working at room temperature and with magnetic field ranging of 1Tesla.

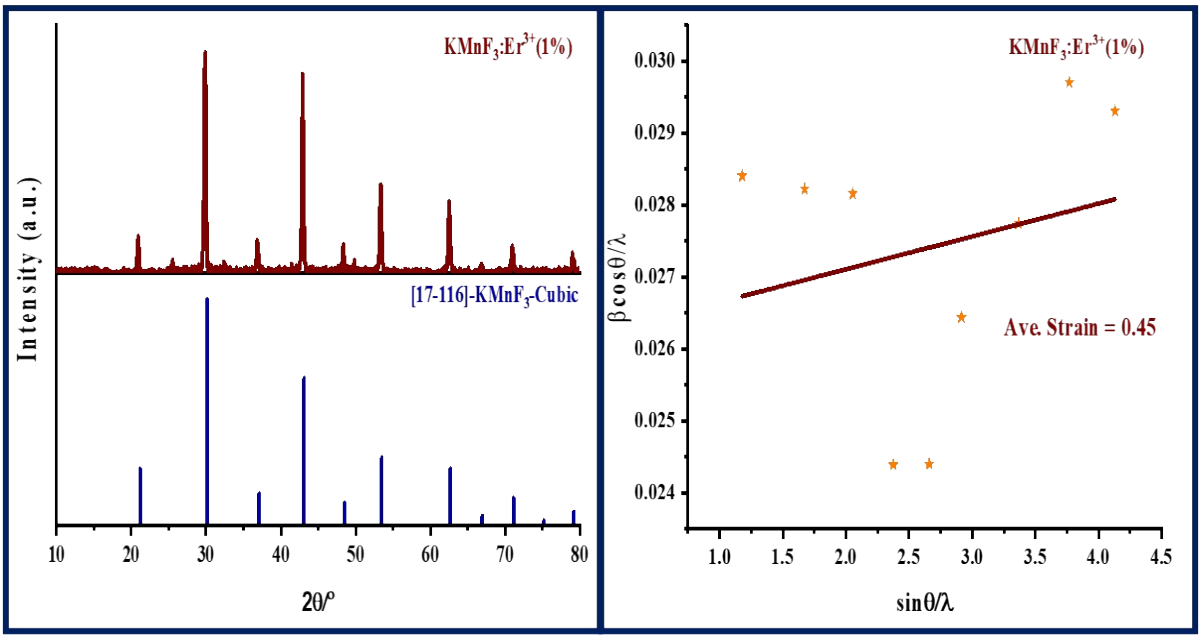

Fig. S1 (i) P-XRD pattern and (ii) lattice strain of $KMnF_3:Er^{3+}$(1%) synthesized at 180 C in a shorter reaction time at microwave–assisted technique with an $[C_4mim]BF_4$ ionic liquid.

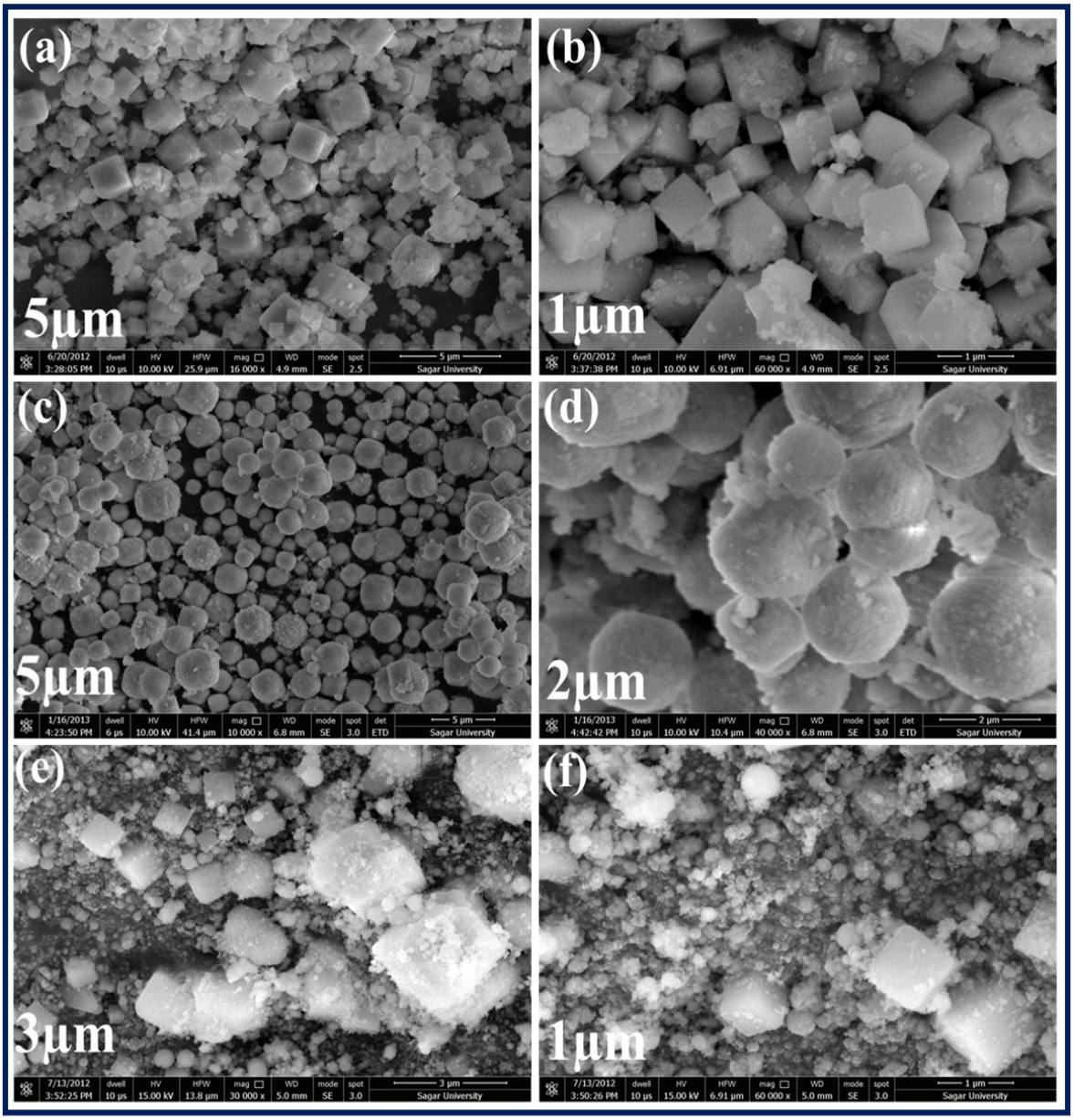

Fig. S2 FE-SEM images of synthesized nanoparticles at different doping concentrations. Panels (a) and (b) show $KMnF_3$ NPs. (c) and (d) represent $KMnF_3:Er^{3+}$(1%)/Yb^{3+}(5%) and panel (e) and (f) for $KMnF_3:Er^{3+}$ (1)/Yb^{3+} (20%) NPs.

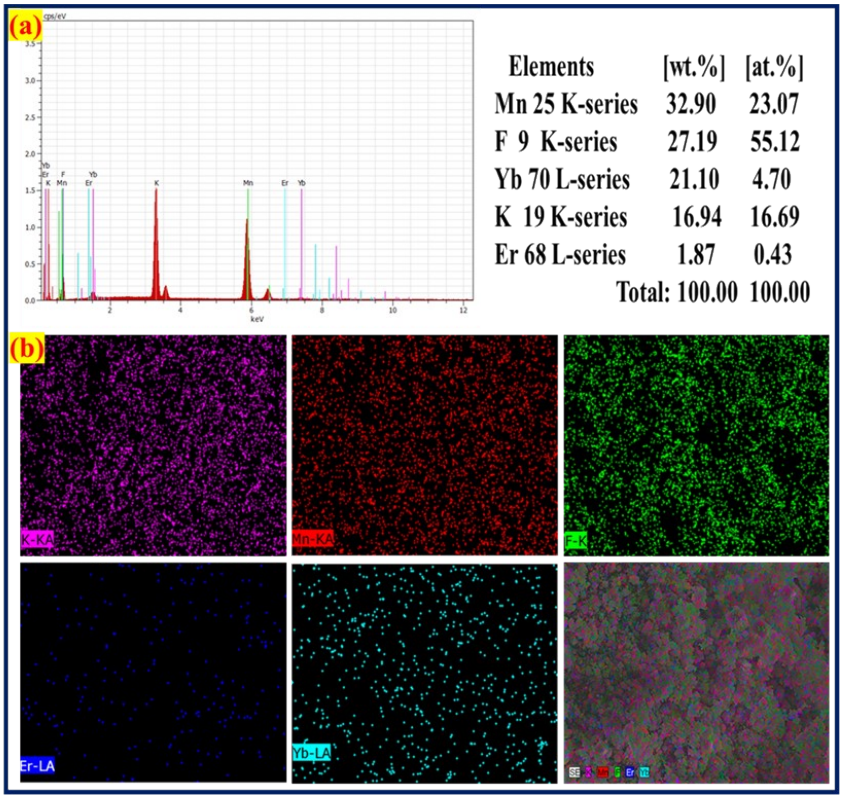

Fig. S3 (a) EDX analysis and (b) elemental mapping of $KMnF_3:Er^{3+}(1\%)/Yb^{3+}(20\%)$ NPs.

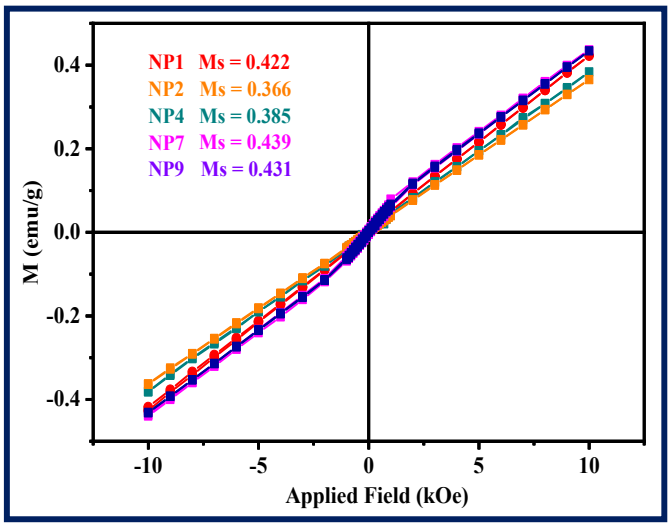

Fig. S4 Magnetization vs applied magnetic field graph of $KMnF_3$ (NP1), $KMnF_3:Er^{3+}(1\%)$ (NP2) $KMnF_3:Er^{3+}(1\%)/Yb^{3+}(5\%)$ (NP4), $KMnF_3:Er^{3+}(1\%)/Yb^{3+}(5\%)$ $Co^{2+}(0.2\%)$ (NP7) $KMnF_3:Er^{3+}(1\%)/Yb^{3+}(5\%)$ $Co^{2+}(1\%)$ (NP9).

References

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2. H. L. Kewat, Y. N. Chouryal, R. K. Sharma, D. J. Mondal, I. A. Wani, A. Waghmare, and P. Ghosh, *ChemistrySelect*, 2024, **9**, e202303750.