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Electronic Supporting Information

Probing emission and defects in $BaW_{1-x}Mo_xO_4$ solid solutions: Achieving color tunable luminescence by W/Mo ratio and size manipulation

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S1. Synthesis of $BaW_{1-x}Mo_xO_4$ solid solutions

For the preparation of samples $Ba(NO_3)_2$, $Na_2WO_4.2H_2O$, $Na_2MoO_4.2H_2O$ and Eu_2O_3 were used as the starting materials. The synthetic procedure is a low temperature polyol method using ethylene glycol as solvent and is same as that we have used in our earlier studies for the preparation of $SrWO_4$ nanocrystalline particles [**1**]. 4 milli moles of $Ba(NO_3)_2$ was dissolved in 25 mL of ethylene glycol by continuous stirring. $Na_2WO_4.2H_2O$ and $Na_2MoO_4.2H_2O$ in the requisite molar ratio, together making 4 milli moles were dissolved in 25 mL of ethylene glycol in a separate beaker. This solution was slowly added to $Ba(NO_3)_2$ solution under continuous stirring. The solution turned white and turbid slowly. The stirring continued overnight and the solution was centrifuged to collect the white precipitate. The precipitate was washed with excess methanol and dried under IR lamp.

For preparing Eu^{3+} doped samples, Eu_2O_3 was dissolved in con. HNO_3 to convert to nitrate, evaporated to dryness and a stock solution was made in water. Required amount of this solution (~ 1mL) corresponding to 2 mol % Eu^{3+} with respect to Ba was added to ethylene glycol solution of $Ba(NO_3)_2$ before the addition of molybdate-tungstate solution. These samples are called henceforth called '*as prepared*' samples and are nanocrystalline particles of $Ba(WO_4)_x(MoO_4)_{1-x}$. A portion of each sample is annealed in a furnace at 500 °C for 6 hours

in air and the resultant samples are henceforth referred to as '*annealed*' samples and correspond to microparticles of $Ba(WO_4)_x(MoO_4)_{1-x}$.

S2. Characterization

Powder X-ray diffraction (PXRD) measurements were carried out using a bench top AXRD (Proto make diffractometer) using Cu Kα of λ=1.5405 Å as monochromatic X-ray source. The diffraction pattern was recorded in the 2θ range of 20 to 80° at a scan rate of 2 deg per minute. Rietveld refinement of the XRD pattern has been carried out using FULLPROF [**2**] software. The instrumental parameters have been obtained from the XRD pattern of LaB_6. A sixth order polynomial was used to describe the background in XRD spectra. The atomic positions were taken from *Kunti et al.,* [**3**] and initial values of lattice parameters were taken from ICDD No. 01-083-6705 for $BaMoO_4$ and 01-082-2636 for $BaWO_4$.

Positron annihilation lifetime spectra were acquired using a spectrometer consisting of a plastic scintillation detector and a lanthanum bromide detector, and having effective time resolution of 265ps. The positron source was 15 μCi carrier free Na-22 deposited and encapsulated between two polyimide films of 8-micron thickness. The positron source was immersed completely in the powder samples and the positron lifetime spectra were acquired. Spectrum of each sample has one million counts. The fraction of positron annihilating in the Na-22 source and encapsulating polyimide films was estimated by using silicon as reference. PALSFit [**4**] was used to fit the positron annihilation lifetime spectra. Theoretical calculation of the positron lifetime in various kinds of defects expected in $BaWO_4$ and $BaMoO_4$ were carried out using MIKA Doppler software [**5**]. For this, a 4×4×4 super cell of $BaWO_4$ or $BaMoO_4$ as the case may be, was considered and the electron density was taken as that from the atomic superposition with electron-positron correlation within the generalized gradient approximation [**6**]. For accounting the enhancement factor, Arponen-Pajanne-Barbiellini approximation was used [**7**]. No relaxation of atoms around the defects was considered in these calculations and the lattice parameters were taken from ICDD numbers mentioned above.

Photoluminescence (PL) measurements were carried out using CD-920 instrument of Edinburgh analytical make and equipped with M-300 monochromators. The excitation source was Xenon flash lamp (μF2, power-100 Watt, Edinburgh make) with frequency range of 10-100 Hz. The PL lifetime measurements were carried out at lamp frequency of 10 Hz. Emission and excitation spectra are recorded with a step of 1nm and about five scans were taken for each spectrum.

S3. Results

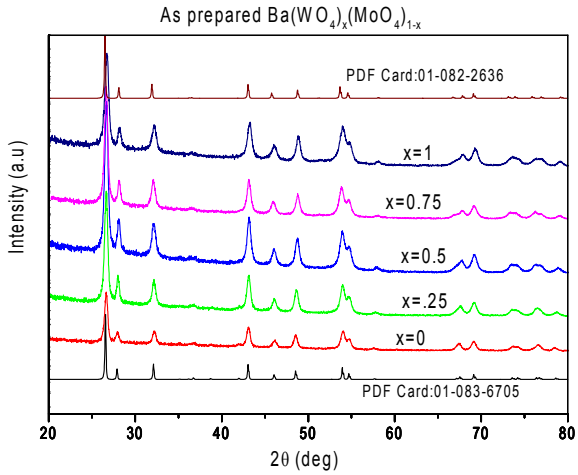

Fig. S1a. Powder XRD patterns of '*as prepared*' undoped $Ba(WO_4)_x(MoO_4)_{1-x}$ samples

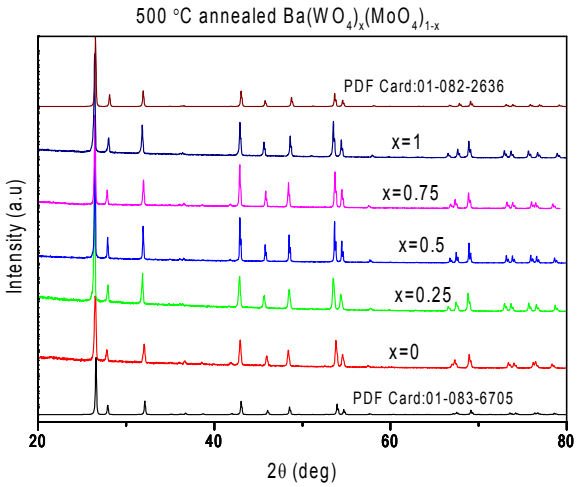

Fig. S1b. Powder XRD patterns of undoped $Ba(WO_4)_x(MoO_4)_{1-x}$ samples *annealed* at 500 °C for 6 hours

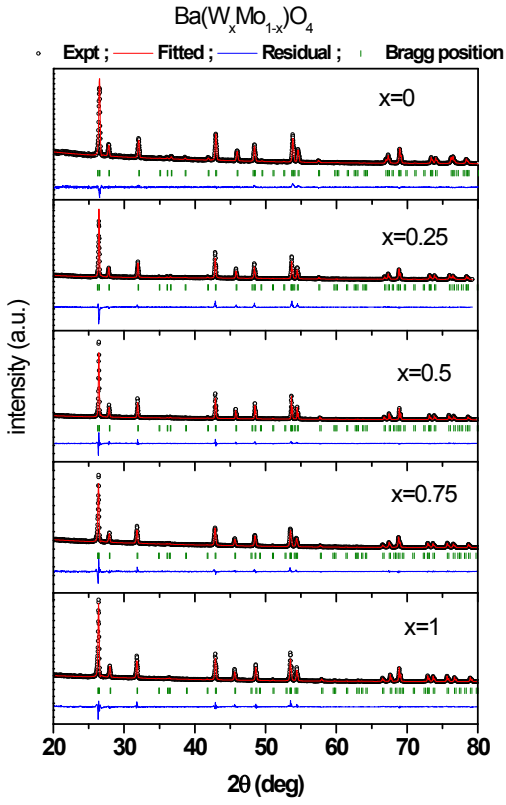

Fig. S2a. Rietveld analysis of XRD patterns corresponding to annealed samples of

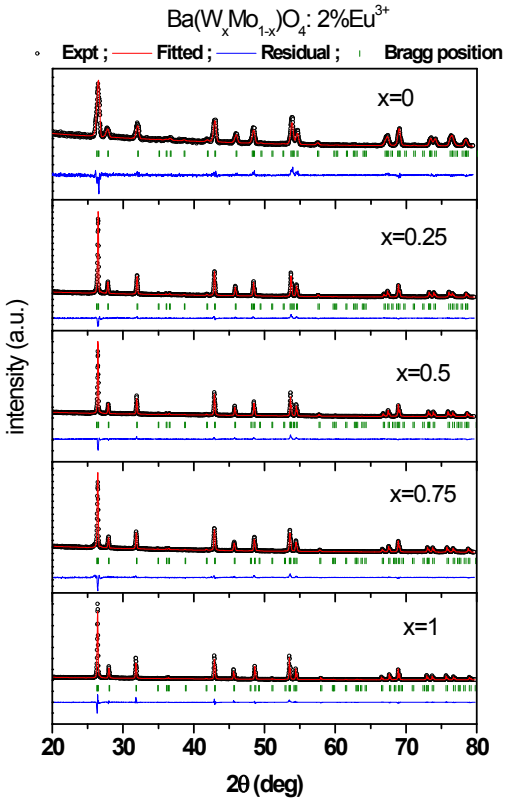

Fig. S2b. Rietveld analysis of XRD patterns corresponding to annealed samples of 2%

$Ba(WO_4)_x(MoO_4)_{1-x}$ Eu^{3+} doped $Ba(WO_4)_x(MoO_4)_{1-x}$

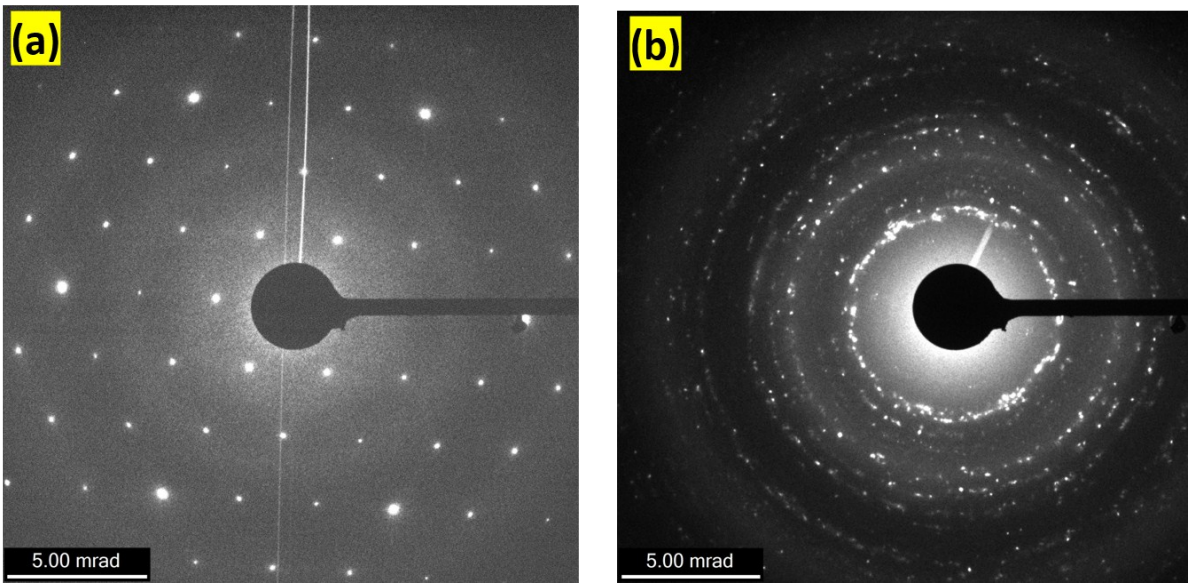

Figure S3: SAED patterns of '*as prepared'* 2% Eu^{3+} doped samples of *(a)* $BaWO_4$ *and (b)* $BaW_{0.50}Mo_{0.50}O_4$

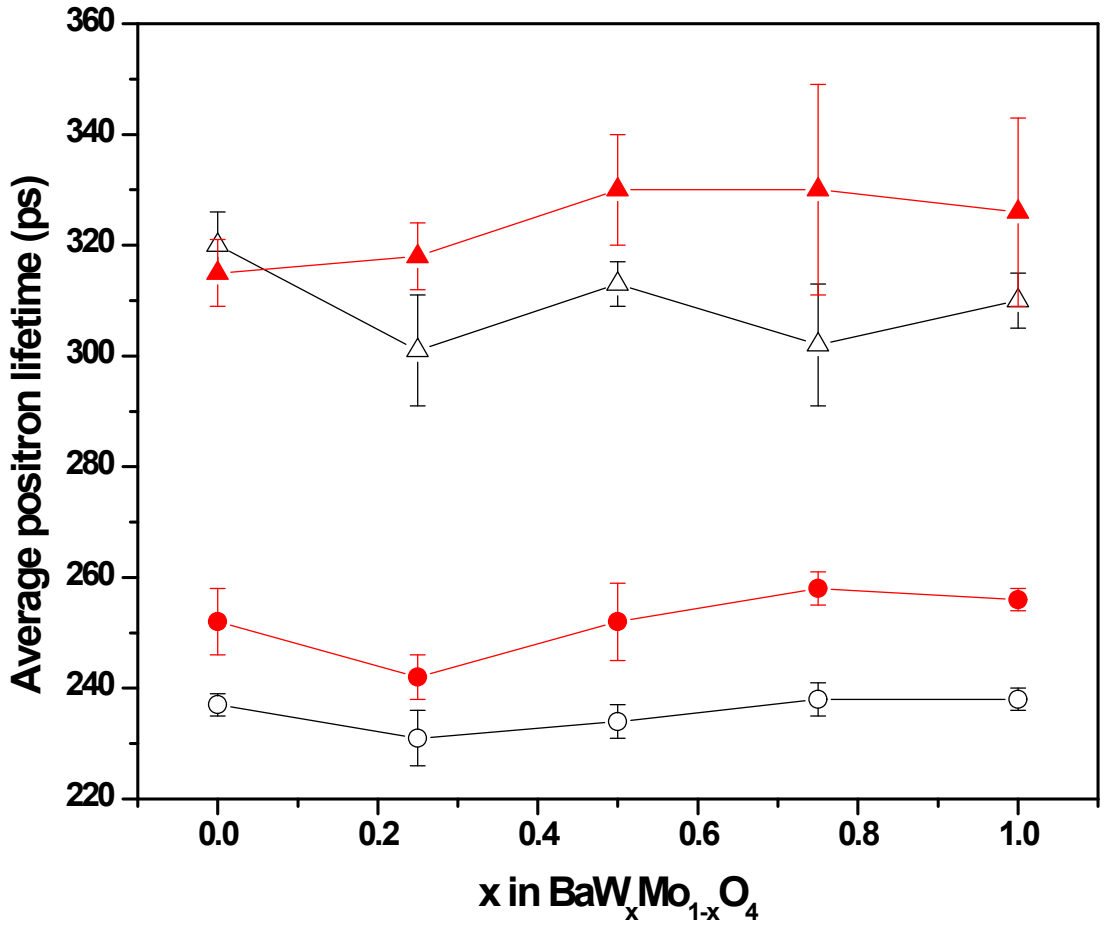

Figure S4. Average positron lifetimes in $BaW_xMo_{1-x}O_4$ samples. Open symbols indicate undoped samples while filled symbols indicate Eu^{3+} doped symbols. Triangles indicate '*as prepared*' nanocrystalline particles while circles indicate samples annealed at 500 °C.

S3.1. Photoluminescence studies on undoped sample

The emission spectra of all the undoped samples are recorded at excitation wavelength of 250 nm. The wavelength has been chosen as corresponding to band to band transitions in tungstate and molybdates. The emission spectra of the nanocrystalline (*as prepared*) and the bulk samples (annealed) of $Ba(WO_4)_x(MoO_4)_{1-x}$ are shown in *Figures S5*. In our earlier studies on the emission from solid state synthesized $BaWO_4$, two broad emission bands centered on ~ 425 nm and 540 nm were observed [**8**] and attributed to charge transfer transition (CTT) within WO_4^{2-} cluster and defects, respectively. The present emission spectra of annealed $BaWO_4$ samples quite like our earlier studies. Luo *et al.* [**9**], in their studies on $BaMoO_4$, have attributed broad emission band below 550 nm to CTT in MoO_4^{2-} while the emission beyond 550 nm is attributed to defects. In the present case, besides the CTT band and emission at higher

wavelengths is seen in all the samples. On the similar analogy, besides the CTT band centered on 420-440 nm, the emission at higher wavelength is likely to be due to various kinds of defects present in the samples. Finer attributions of emissions to various kinds of defects needs investigation via theoretical calculations and low temperature emission measurements.

The relative emission intensities, taken as integrated areas under the emission curves in ***Figure S5***, from all the undoped samples are given as ***Figure S6a.*** In the bulk samples, the integral area under the emission spectrum is maximum in the case of $W_{0.50}Mo_{0.50}$ sample. The minimum emission intensity was found in case of $W_{0.25}Mo_{0.75}$ sample. The difference in emission intensity with W/Mo concentration is more obvious in nanocrystalline samples compared to bulk. Among the nanocrystalline samples, maximum overall intensity as well as higher intensity beyond 500 nm was found in $W_{0.75}$ sample, which also showed higher fraction of positrons annihilating from defects or higher defect density.

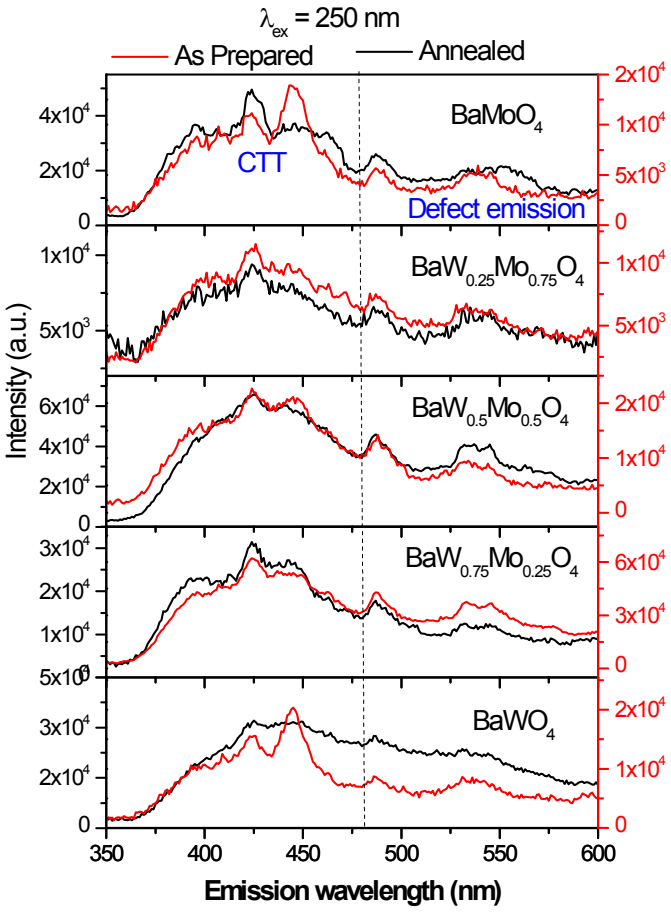

Figure S5: Photoluminescence emission spectra of as *prepared* (nanocrystalline) and annealed (bulk) samples of undoped $BaW_xMo_{1-x}O_4$ with λ_{ex} of 250 nm.

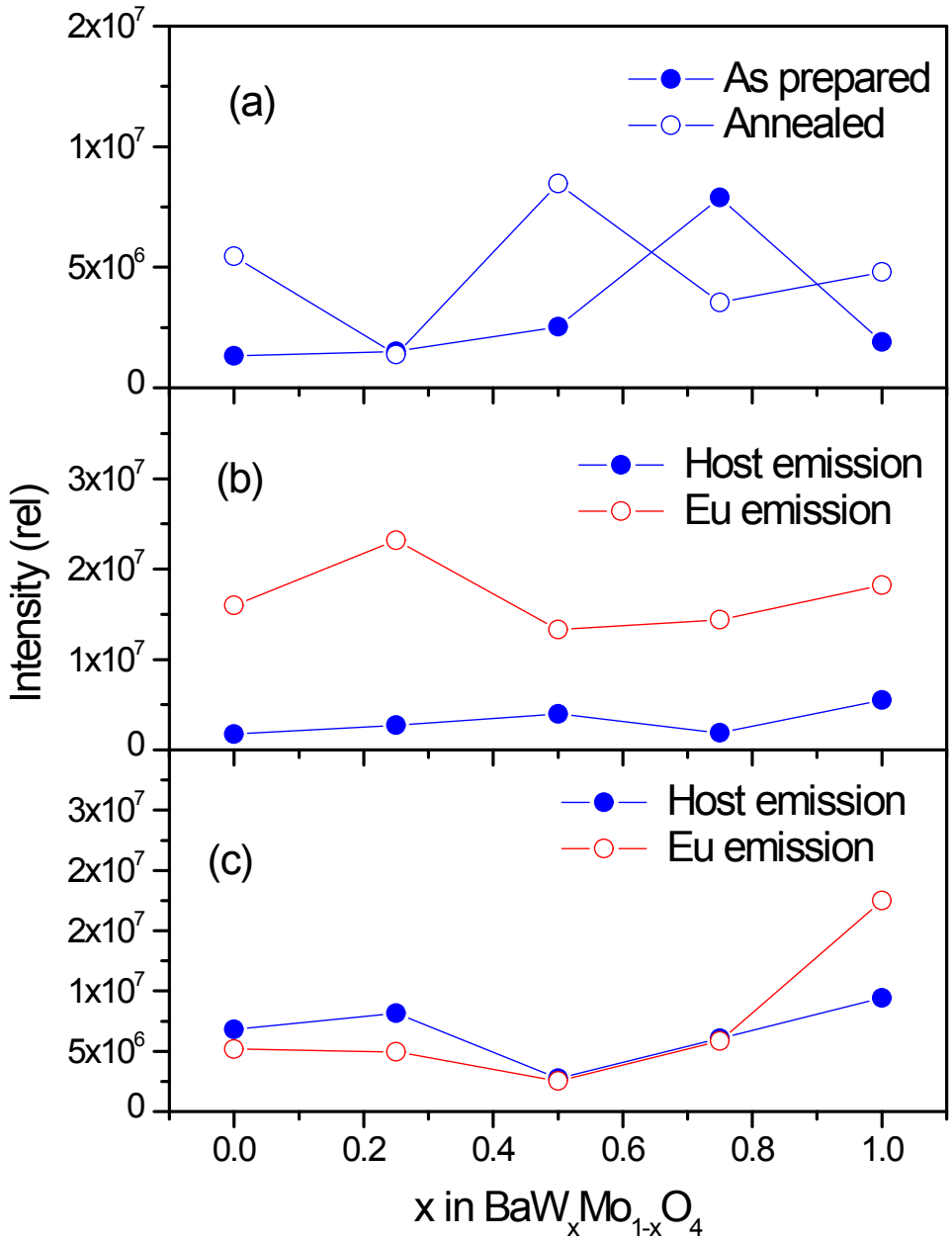

Figure S6. (a) Relative host emission intensities in undoped *'as prepared'* and annealed $BaW_xMo_{1-x}O_4$ samples (b) Relative intensities of host emission (< 575 nm) and Eu^{3+} emission (575 -675 nm) in as prepared (nano) Eu^{3+} doped $BaW_xMo_{1-x}O_4$ samples (c) Relative intensities of host emission (< 575 nm) and Eu^{3+} emission (575 -675 nm) in annealed (bulk) Eu^{3+} doped $BaW_xMo_{1-x}O_4$ samples

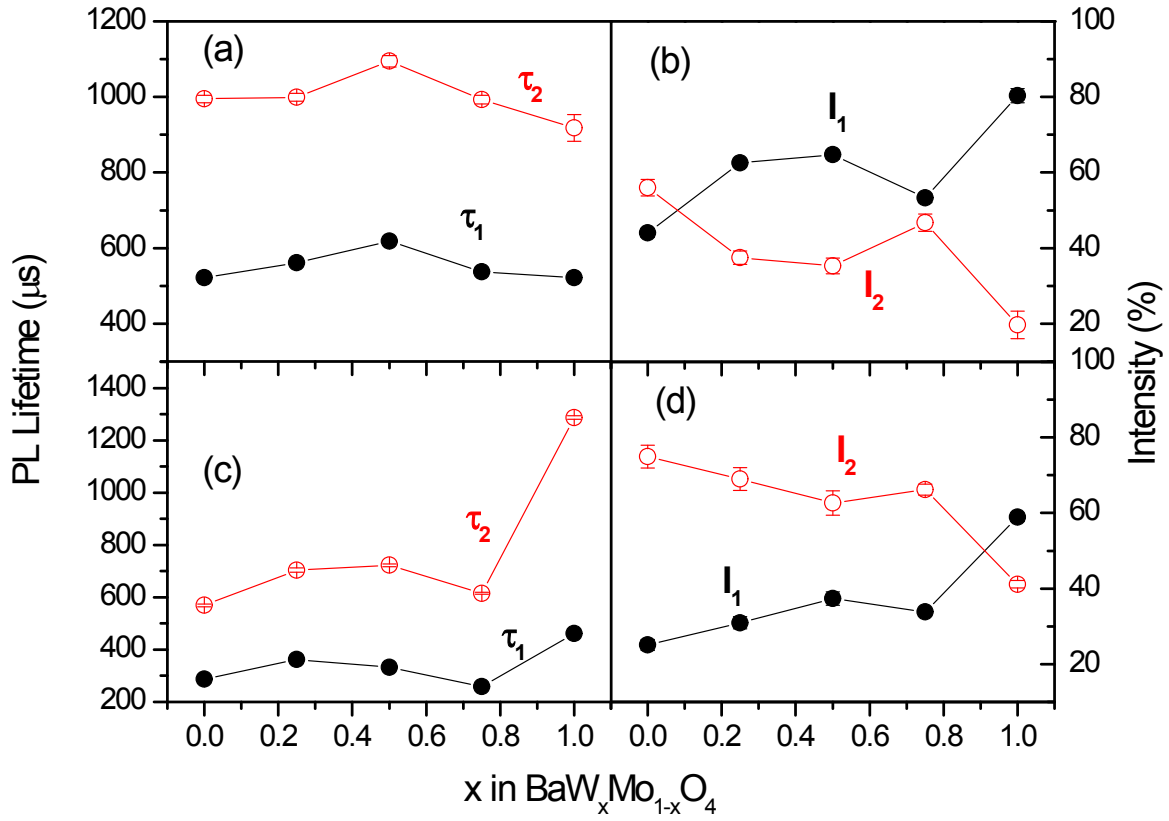

Figure S7. Photoluminescence lifetimes and their relative intensities for the emission of 618 nm in 2% Eu^{3+} doped $BaW_xMo_{1-x}O_4$. The PL data of as prepared samples are in (a) and (b) while the same for annealed sample at 500 °C are in (c) and (d). Filled symbols correspond to shorter of the two lifetime components and its intensity, and open symbols correspond to the longer of the two components and its intensity.

S4. References

1. S.K. Gupta, K. Sudarshan, P.S. Ghosh, K. Sanyal, A. P. Srivastava, A. Arya, P. K. Pujari and R. M. Kadam, Luminescence of undoped and Eu^{3+} doped nanocrystalline $SrWO_4$ scheelite: time resolved fluorescence complimented by DFT and positron annihilation spectroscopic studies, *RSC Adv.,* 2016, **6**, 3792.
2. Fullprof JR-c. A program for Rietveld, Profile matching and integrated intensity refinements for X-ray and neutron data. Version; 2000.
3. A.K. Kunti, N. Patra, S.K. Sharma, H.C. Swart, Radiative transition probability enhancement of white light emitting Dy^{3+} doped and K^+ co-doped $BaWO_4$ phosphors via charge compensation, *Journal of Alloys and Compounds, 2018,* **735**, 2410-2422
4. P. Kirkegaard, J.V. Olsen, M.M. Eldrup, N.J. Pedersen,. PALSfit: A computer program for analyzing positron lifetime spectra, Risø National Laboratory for Sustainable Energy Technical University of Denmark, 2009, Riso-Report, No. 1652(EN)
5. Filip Tuomisto and Ilja Makkonen, Defect identification in semiconductors with positron annihilation: Experiment and theory, Rev. Mod. Phys. 2013, 85, 1583-1631.
6. M.J. Puska, and R.M. Nieminen, Defect spectroscopy with positrons: a general calculational method. *Journal of Physics F: Metal Physics*, 1983, **13**(2), 333-346.
7. B. Barbiellini, M. J. Puska, T. Torsti, and R. M. Nieminen, Gradient correction for positron states in solids, *Physical Review B* 1995, ***51***, 7341(R).

8. C.S. Datrick, K. Sudarshan, Santosh K. Gupta, P. Nandi, Role of energy transfer, defect and lattice dimension in photophysical characteristics of $AWO_4:Nd^{3+}$ (A=Ca, Sr and Ba), *J. Am. Ceram. Soc.* 2020, DOI: https://doi.org/10.1111/jace.17197
9. Z. Luo, H. Li, H. Shu, K. Wang, J. Xia, and Y. Yan, Synthesis of BaMoO4 nestlike nanostructures under a new growth mechanism, *Crystal Growth & Design*, 2008, **8,** 2275-2281.