Supporting Information (S1) for

Structural and Photoluminescence Properties of Stannate based Displaced Pyrochlore-type Red Phosphors: $Ca_{3-x}Sn_3Nb_2O_{14}$: $x$$Eu^{3+}$

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ES1. Calculation of Quantum Efficiency of Red Phosphors

Assuming that only radiative and non radiative processes are essentially involved in the depopulation of $^5D_0$ states of Eu^{3+} ion, the quantum efficiency (η) can be expressed as;

$$\eta = A_{rad} / (A_{rad} + A_{nrad}) \quad (1)$$

where A_{rad} and A_{nrad} are the radiative and non-radiative transition probabilities respectively. The emission intensity (I) can be calculated as the integral intensity S of $^5D_0$-$^7F_{0-4}$ emission curves as;

$$I_{i-j} = \hbar\omega_{i-j} A_{i-j} N_i \sim S_{i-j} \quad (2)$$

where i and j are the initial level ($^5D_0$) and the final levels ($^7F_{0-4}$), respectively; $\hbar\omega_{i-j}$ is the transition energy, A_{i-j} is the Einstein's coefficient of spontaneous emission, and N_i is the population of the $^5D_0$ emitting level.

The experimental coefficients of spontaneous emission were then calculated according to the equation;

$$A_{0j} = A_{01} (I_{0j} / I_{01}) (\nu_{01} / \nu_{0j}) \quad (3)$$

where ν_{01} and ν_{0j} are the energy baricenters of the $^5D_0$-$^7F_1$ and $^5D_0$-^7F_jenergy levels determined from the emission peak of Eu^{3+} ion. A_{01} is the Einstein's coefficient of spontaneous emission between $^5D_0$ and $^7F_1$ energy levels.

In vacuum, the average refractive index (n) is 1.506 and $(A_{0-1})_{vac} = 14.64 s^{-1}$ is considered. Then the value of A_{0-1} was expressed as,

$$A_{0-1} = n^3 (A_{0-1})_{vac} \sim 50 s^{-1} \tag{4}$$

The life time (τ) of the $^5D_0$ states, A_{rad} and A_{nrad} are related as;

$$A_{tot} = 1/\tau = A_{rad} + A_{nrad} \tag{5}$$

ES1. Calculation of Spectral Parameters

The Judd-Ofelt intensity parameters and the spectral parameters of the $Ca_{3-x}Sn_3Nb_2O_{14}$:$x$$Eu^{3+}$ (x= 0.05, 0.10, 0.15, and 0.20) phosphors tabulated in Table 4 of the manuscript is calculated from the emission spectrum for Eu^{3+} ion based on the $^5D_0 \rightarrow {}^7F_2$ and $^5D_0 \rightarrow {}^7F_4$ transitions and $^5D_0 \rightarrow {}^7F_1$ magnetic dipole allowed transitions as the reference. The integrated emission intensities associated with the radiative emission rates can be written as:

$$\frac{A_{0-2,4}}{A_{0-2,4}} = \frac{I_{0-2,4} h\nu_{0-2,4}}{I_{0-2,4} h\nu_{0-2,4}} \tag{6}$$

where I_{0-J} is the integrated emission intensity and $h\nu_{0-J}$ is the energy corresponding to transition$^5D_0 \rightarrow {}^7F_J$ (J = 1, 2, 4). The transition $^5D_0 \rightarrow {}^7F_J$ is left out due to their small emission intensities. The magnetic dipole radiative emission rate A_{0-1}has a value of ≈50 s^{-1}. The radiative emission rates $A_{0-2,4}$ are related to forced electric dipole transitions and they may be written as a function of the J–O intensity parameters:

$$A_{0-J} = \frac{64\pi^4(\nu_{0-2,4})^3 e^2}{3hc^3}\frac{1}{4\pi\epsilon_0}\chi \sum_{j=2,4,6} \Omega_j < \langle 5D_0 \,|\, U^{(J)} \,|\, 7F_{2,4} > \rangle^2 \quad (7)$$

where, χ is the Lorentz local field correction factor given as function of the index of refraction n of the host χ = n(n2+ 2)$^{2/9}$. The non-zero square reduced matrix elements are solely $< \langle 5D_0 \,|\, U^{(2)} \,|\, 7F_2 > \rangle^2$=0.0032 and $< \langle 5D_0 \,|\, U^{(4)} \,|\, 7F_4 > \rangle^2$= 0.0023. Thus, using Eqs (6) and (7) the values of $\Omega_{2,4}$ were obtained.[1] The value of Ω_6 could also be estimated by analyzing the$^5D_0 \rightarrow {}^7F_6$transition but in the present case, this emission could not be observed. The calculated Judd–Ofelt parameters have been used to predict some important radiative properties such as transition probabilities, radiative lifetime and branching ratios and lifetimes for the excited states of Eu^{3+}ions.The radiative transition probability for a transition $\Psi J \rightarrow \Psi' J'$ can be calculated from Eq. (3) as $A_{rad}(\Psi J,\ \Psi' J') = A_{J-J'}$.

The total radiative transition probability (A_T) can be calculated using the equation below:

$$A_T(\Psi J) = \Sigma_{J'} A_{J-J'} \quad (8)$$

The radiative lifetime $\tau_{rad}\,(\Psi J)$ of an excited state in terms of A_T, is given by:

$$\tau_{rad}\,(\Psi J) = \frac{1}{A_T(\Psi J)} \quad (9)$$

The branching ratio $\beta(\Psi J)$ corresponding to the emission from an excited level to its lower levels is given by:

$$\beta(\Psi J) = \frac{1}{A_T(\Psi J)} \quad (10)$$

The stimulated emission cross-section ($\sigma(\lambda_p)$) can be expressed as:

$$\sigma(\lambda_p)(J \rightarrow J') = \frac{\lambda_p^4}{8\pi c n^2 \Delta\lambda_{eff}} A_{rad}(J \rightarrow J') \quad (11)$$

where λ_p is the peak wavelength and $\Delta\lambda_{eff}$ is its effective line width found by dividing the area of the emission band by its maximum height.

Figure Captions

Fig. S1. Scanning electron micrographs of $Ca_{3-x}Sn_3Nb_2O_{14}$:$x$$Eu^{3+}$: (a) x= 0.05, (b) x= 0.10, (c) x= 0.15 and (d) x=0.20.The particles appear to be highly crystalline and are slightly agglomerated. The particles are in the scale of 1-5µm in size with homogeneous nature.

Fig. S2. EDS spectra of $Ca_{3-x}Sn_3Nb_2O_{14}$:$x$$Eu^{3+}$: (a) x= 0.05, (b) x= 0.10, (c) x= 0.15 and (d) x=0.20. EDS quantification with Eu^{3+} concentration confirms the increase of oxygen content in the lattice.

Fig. S1

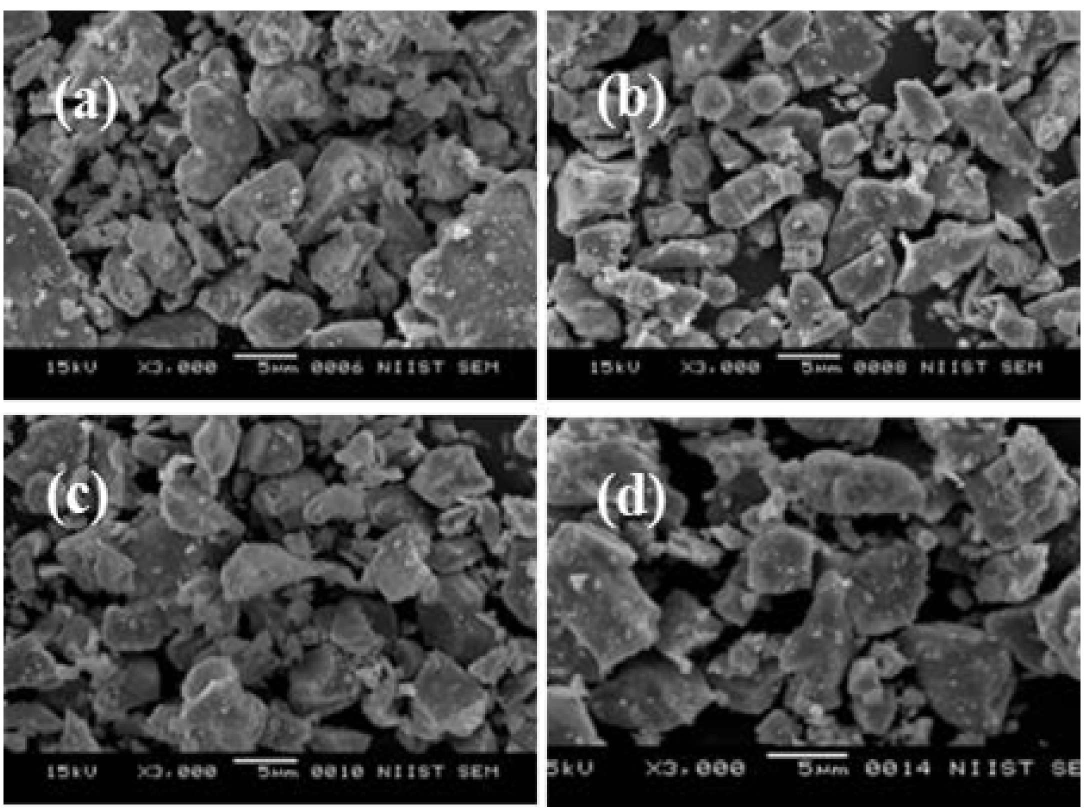
(a)
15kV X3,000 5μm 0006 NIIST SEM
(b)
15kV X3,000 5μm 0008 NIIST SEM
(c)
15kV X3,000 5μm 0010 NIIST SEM
(d)
5kV X3,000 5μm 0014 NIIST SE

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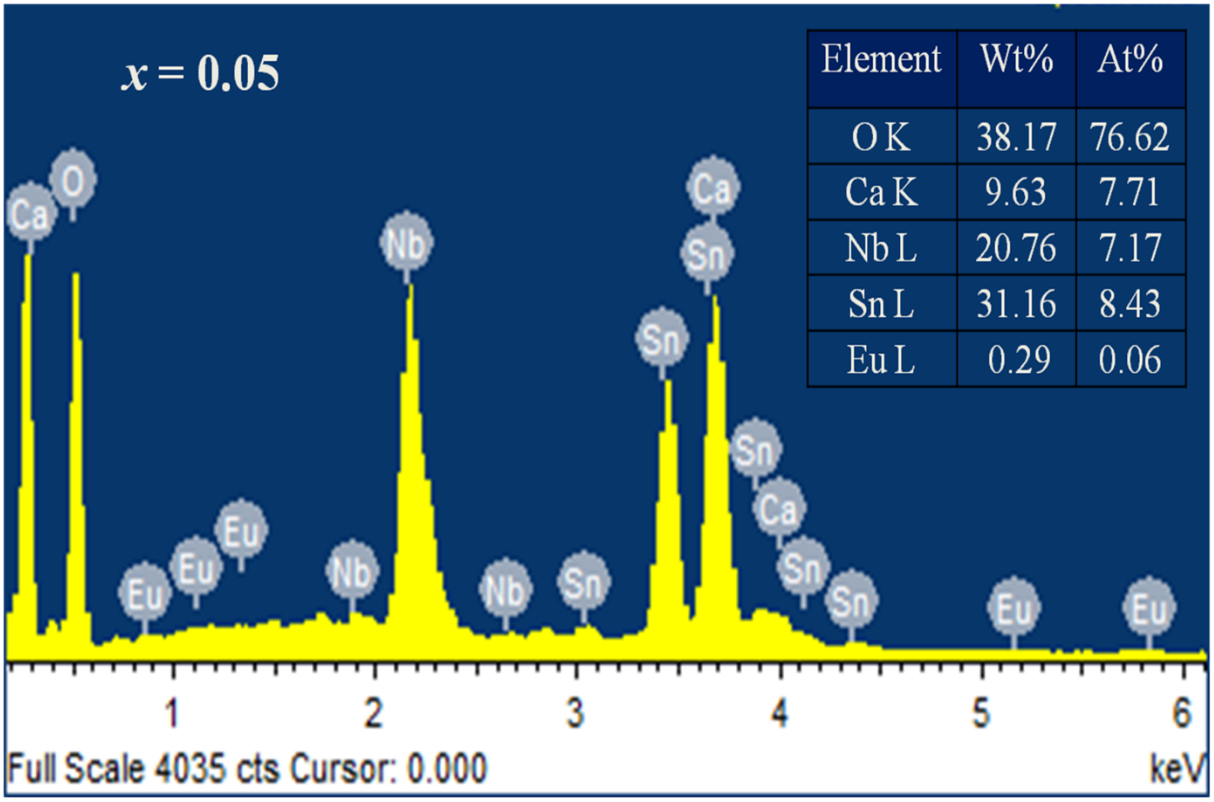
Fig. S2.

(a)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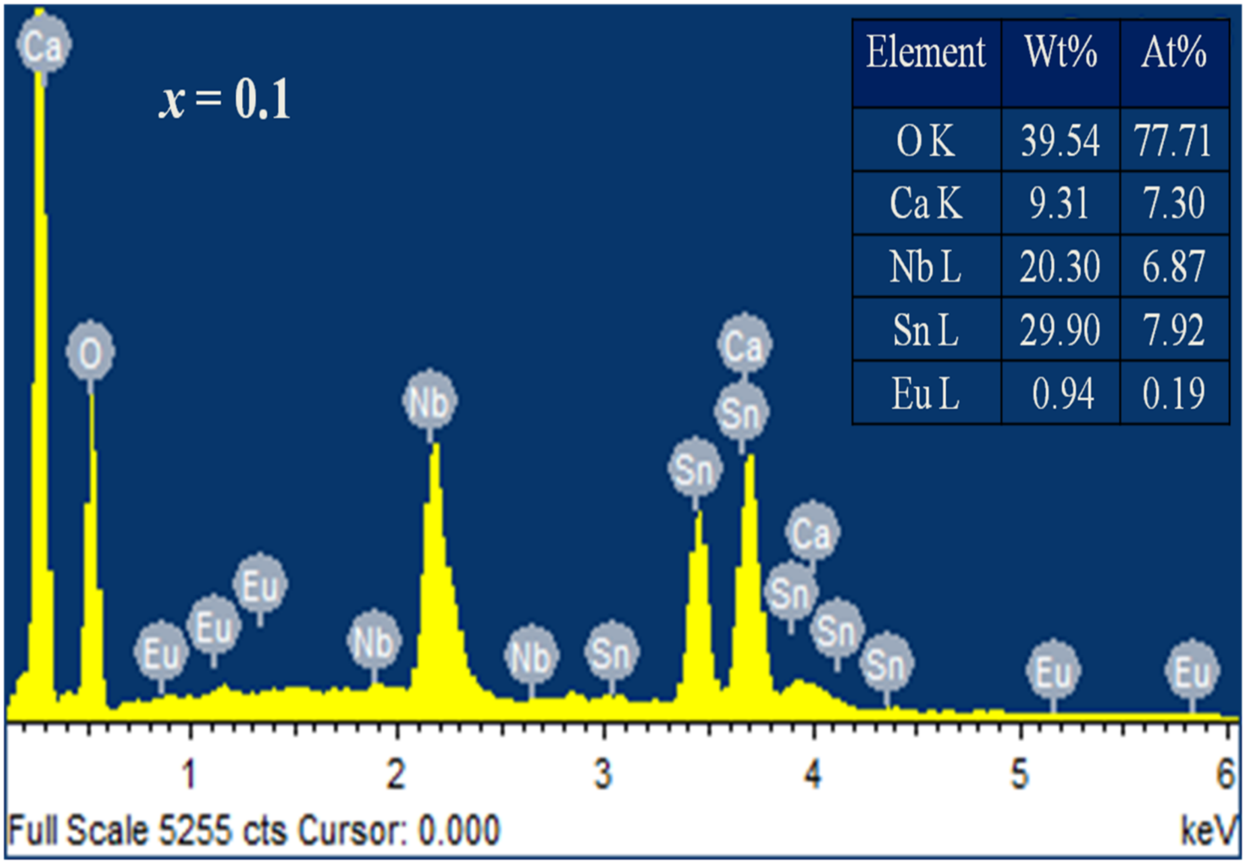
O K 38.17 76.62
Ca K 9.63 7.71
Nb L 20.76 7.17
Sn L 31.16 8.43
Eu L 0.29 0.06
Ca
O
Nb
Sn
Eu
1
2
3
4
5
6
Full Scale 4035 cts Cursor: 0.000
keV

(b)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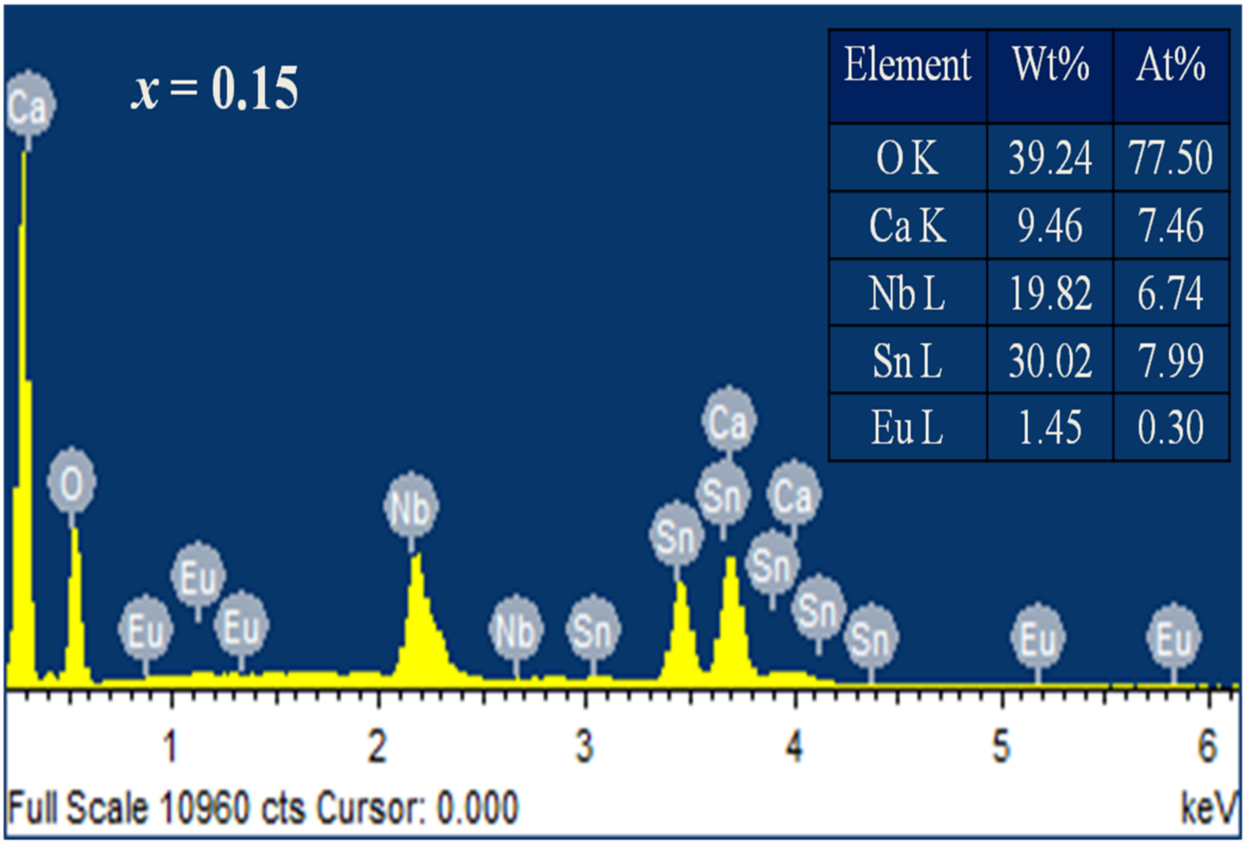
Element
Wt%
At%
O K
39.54
77.71
Ca K
9.31
7.30
Nb L
20.30
6.87
Sn L
29.90
7.92
Eu L
0.94
0.19
Ca
O
Nb
Sn
Eu
1
2
3
4
5
6
Full Scale 5255 cts Cursor: 0.000
keV

(c)


x = 0.15
Element Wt% At%
O K 39.24 77.50
Ca K 9.46 7.46
Nb L 19.82 6.74
Sn L 30.02 7.99
Eu L 1.45 0.30
Ca
O
Eu
Eu
Eu
Nb
Nb
Sn
Sn
Sn
Ca
Sn
Ca
Sn
Sn
Eu
Eu
1 2 3 4 5 6
Full Scale 10960 cts Cursor: 0.000
keV

(d)

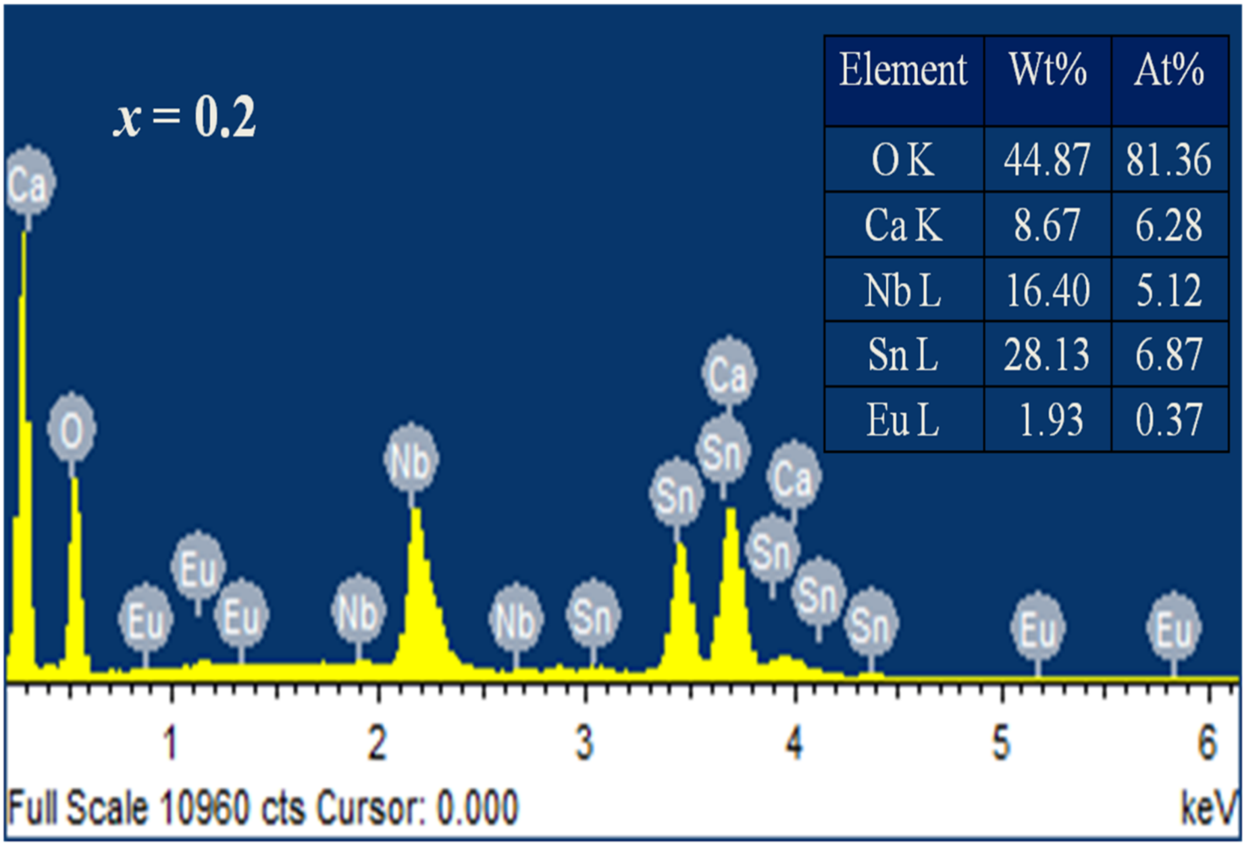


Fig. S2 EDS spectra of $Ca_{3-x}Sn_3Nb_2O_{14}$:$x$$Eu^{3+}$: (a) x= 0.05, (b) x= 0.10, (c) x= 0.15 and (d) x=0.20. EDS quantification with Eu^{3+} concentration confirms the increase of oxygen content in the lattice.