Inorganic Chemistry Cite This: Inorg. Chem. XXXX, XXX, XXX-XXX

Article pubs.acs.org/IC

Deciphering the Role of Charge Compensator in Optical Properties of SrWO₄:Eu³⁺:A (A = Li⁺, Na⁺, K⁺): Spectroscopic Insight Using Photoluminescence, Positron Annihilation, and X-ray Absorption

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Supporting Information

ABSTRACT: Studies have been carried out to understand the specific role of the alkali charge compensator on the luminescence properties of an alkali ion (Li⁺, Na⁺, and K⁺) codoped SrWO4:Eu phosphor. The oxidation state of the europium ion was found to be +3 on the basis of X-ray absorption near edge structure (XANES) measurements. This is the first report of its kind where opposite effects of Li⁺ ion and Na⁺/K⁺ ions on photoluminescence intensity have been observed. Li⁺ ion codoping enhanced the photoluminescence intensity from SrWO₄:Eu³⁺ phosphor while Na⁺/K⁺ ion codoping did not. On the other hand, the luminescence lifetime is maximum for the Na⁺ ion codoped sample and minimum for the Li⁺ ion codoped sample. The results could be explained successfully using time-resolved luminescence, positron annihilation lifetime spectroscopy



(PALS), and extended X-ray absorption fine structure (EXAFS) spectroscopy measurements. Changes in the Eu-O bond length and Debye–Waller Factor (σ^2) upon Li⁺/Na⁺/K⁺ codoping were monitored through EXAFS measurements. PALS also highlighted the fact that Li⁺ codoping is not contributing to reduction in the cation vacancies and might be occupying interstitial sites rather than lattice positions due to its very small size. On europium doping there is lowering in symmetry of SrO₈ polyhedra from S_4 to C_{6i} which is reflected in an intense electric dipole transition in comparison to the magnetic dipole transition. This is also corroborated using trends in Judd-Ofelt parameters. The results have shown that the luminescence lifetime is better when the vacancy concentration is lower as induced by Na^+ and K^+ codoping, while the emission intensity is higher in the samples when distortion around Eu³⁺ is reduced as induced by Li⁺ codoping.

1. INTRODUCTION

Europium-based luminescence materials are extensively used in solid-state lighting, radiometric luminescent thermometers,¹ solar cells,^{2,3} downconversion luminescence and photocatalysis,^{4,5} and photothermal chemotherapy⁶ and as spectroscopic^{7,8} and analytical probes.⁹ Directly populating the excited state of the europium ion is difficult mainly because of the low absorption coefficient of the f-f transition due to its parity-forbidden nature. This can be taken care of either by ligand-sensitized fluorescence or by doping the europium ion in a suitable inorganic host. In this context hosts play an important role in optimal applications. The prerequisite properties of a good luminescence host are that it should be thermally and chemically stable, should be easy to synthesize, should not emit corrosive gases on electron bombardment, and should have low phonon energy. Because of their advantageous properties, tungstatebased scheelite structures are some of the most highly explored luminescence hosts and are used for applications such as upconversion¹⁰ and luminescence thermometry¹¹ and as red phosphors,¹² efficient green emitting phosphors,¹³ etc. Among divalent tungstates, SrWO₄ is superior to many others because of its interesting scintillation properties and ability to act as a host wherein both lasing as well as Raman properties can be

explored simultaneously.¹⁴ It belongs to the scheelite family having a tetragonal structure with space group $I4_1/a$ and point group symmetry C_{4h}^6 . The site symmetries of Sr²⁺, W⁶⁺, and O^{2-} ions are S_4 , T_d , and C_1 , respectively.¹⁵ With regard to optoelectronic applications; SrWO₄ is considered an excellent luminescence host owing to size matching of Sr²⁺ ion to the lanthanides, low phonon energy, high thermal and mechanical stability, ease of synthesis, etc. There are various studies related to europium ion doping in $SrWO_4$ and the related photo-luminescence.^{16–21} The structure plays a very important role in the optimum performance of luminescence materials. The presence of defects in the phosphor materials provides an additional path for nonradiative transitions and thus decreases the quantum yield of phosphors. These intrinsic defects are difficult to remove from any material, as they are omnipresent and will drastically deteriorate the performance of the luminescent material.

In order to improve the performance of lanthanide-based downconversion phosphors in various optoelectronics devices and in other technological applications, one needs to enhance the luminescence efficiency of synthesized phosphor materials.

Received: October 31, 2017

There are different ways of achieving this, such as using a sensitizer which can absorb UV light and transfer the energy to lanthanide ion, using host-sensitized energy transfer, complexing with an organic ligand, using other lanthanide codopants, etc.²²

Most of the studies on phosphor materials have highlighted the fact that lattice modification is one of the most sought after techniques for improving the luminescence efficiency of the phosphor.^{23–25} Such modification can be induced by codoping a foreign ion in the lattice which can create defects or alter the local site symmetry of the primary dopant ion and ultimately influence the relaxation phenomenon. The most preferred lattice modifier for enhancing the photoluminescence efficiency is an alkali metal ion because of its low valence state and distinct ionic radius.^{23,26–29} The doped M⁺ can be easily inserted into the doped phosphor host substitutionally or interstitially and can modify the local symmetry around the Ln^{3+} , leading to an increase in luminescence intensity.

From a structural point of view, there should be a charge balance mechanism in replacing A^{2+} by Eu^{3+} ion (a commonly used luminescence activator). In the case of $SrWO_4$, wherein Eu^{3+} goes to the Sr^{2+} site, doping leads to creations of negatively charged strontium ion vacancies (V_{Sr}) for charge compensation. The presence of such defects deteriorates the optical performance of the synthesized phosphor materials. There can be another possibility of charge compensation by interstitial oxygen, but they are more common in wolframite compounds such as PbWO₄, as reported by Peng and co-workers³⁰ and are very rare in alkaline-earth-based scheelite compounds such as CaWO₄, BaWO₄ and SrWO₄.

Jiang et al. have investigated the influence of Li^+ codoping on photoluminescence properties of scheelite $SrWO_4:Eu^{3+}$ phosphor.³⁰ However, the work was restricted to only one alkali-metal ion. i.e. Li^+ , and no effort was made to extend it to Na⁺ and K⁺ codoping.

Ran et al.³¹ have investigated the effect of monovalent alkalimetal ions such as Li, Na, and K on energy transfer efficiency from Bi³⁺ to Eu³⁺ in ZnMoO₄:Eu³⁺:Bi³⁺. Li et al.³² have also studied the effect of Li⁺ ions in the scheelite host CaMoO₄, but they used Dy³⁺ as the activator ion instead of Eu³⁺. Further, in another work, Li et al.³³ extended their observation of the effect of Li⁺, Na⁺, and K⁺ on the PL enhancement of Tb³⁺-codoped CaMoO₄ phosphors. In all of these studies, it is reported in general that codoping of alkali-metal ions enhances the photoluminescence of the phosphors and that the most likely mechanism operating is the reduction in the negatively charged cation vacancy concentration which was expected to arise when lanthanide +3 ions substitute +2 ions in the host lattice. Though it is generally reported that alkali codoping enhances PL intensity, the intensity of emission decreased in ZnTa₂O₆:Pr^{3+ 34} while the emission lifetimes increased. Enhancements in emission were reported to be best upon Na⁺ doping in CaSb₂O₆:Bi^{3+ 35} and BaCaBO3F:Eu3+,36 while Li+ has been found to be a better alkali charge compensator in the case of $Ca_6Ba(PO_4)_4O:Ce^{3+37}$ and $Ca_3Ti_2O_7:Eu^{3+}.^{38}$ K⁺ doping was found to enhance the emission more distinctly in comparison to other alkali ions in the case of $BaMoO_4$: Pr^{3+} .³⁹ As far as the synthesis of europiumdoped tungstate is concerned, various synthesis techniques have been envisaged such as a supersonic microwave coassistance (SMC) method,^{40,41} hydrothermal synthesis,⁴² citrate-nitrate combustion synthesis,⁴³ etc. The studies reported show that the dependence of PL on the nature and concentration of the codoped ion is not unique and the reasons behind these dependencies are not clearly understood.

Moreover, structural characterization of the alkali-codoped phosphors has been limited mainly to X-ray diffraction. We have extended it to synchrotron-based X-ray absorption spectroscopy to correlate the structural changes and to positron annihilation lifetime spectroscopy (PALS) to understand the defects. The role of alkali-metal codoping on photoluminescence properties and the observed differences were correlated with structural changes and defect concentrations. None of the existing literature has given such complete information on role of charge compensator and the mechanism for emission enhancement. An effort was made to investigate the energy transfer efficiency from the host to the europium ion as a function of codopant ion. Judd–Ofelt analysis was carried out to investigate the radiative transition rate, Judd–Ofelt parameters, and quantum efficiency for each sample.

This study was carried out with the objective of understanding changes in $SrWO_4:Eu^{3+}$ upon alkali doping that are responsible for the optical properties of the phosphor. The effect of alkali ion doping on the defect chemistry, photophysical properties, and structural properties in $SrWO_4:Eu^{3+}$ phosphor has been studied using positron annihilation lifetime spectroscopy (PALS), time-resolved photoluminescence spectroscopy (TRPLS), and extended X-ray absorption fine structure (EXAFS). A plausible mechanism for luminescence enhancement on alkali ion codoping and the different behavior by each ion is discussed. In the present study we have performed X-ray absorption near edge structure (XANES) and EXAFS spectroscopy on the SrWO₄:Eu³⁺:M⁺ system to elucidate the oxidation state of europium ion and to probe the local structure surrounding Eu ions, respectively.

2. EXPERIMENTAL SECTION

2.1. Synthesis of SrWO₄:Eu³⁺:M⁺ Phosphor (M = Li, Na, K). SrCO₃ (Analytical Reagent grade, Chemico Fine Chemicals, Mumbai, India), WO3 (Analytical Reagent grade, SD Fine Chemicals, Mumbai, India), Eu₂O₃ ((99.999%, SPEX Industries, Inc., USA), Li₂CO₃, Na2CO3, and K2CO3 were used in the synthesis. The synthesis of SrWO₄ was carried out by a solid-state route. For this 2×10^{-3} mol each of SrCO₃ and WO₃ were well mixed and sintered at 900 °C for 6 h and then at 1300 °C for 6 h with intermediate grinding. Europiumdoped samples were prepared for notional replacement of 2% Sr²⁺ sites with Eu³⁺ doping. For europium doping, 1.94 mmol of SrCO₃ and 0.2 mmol of Eu_2O_3 (0.4 mmol of Eu^{3+}) were mixed with 2 mmol of WO3 and sintered as in the case of undoped samples. The stoichiometry was chosen as 2 mol of Eu³⁺ would charge compensate for 3 mol of Sr²⁺. For the charge compensation by alkali doping, 0.2 mmol of M_2CO_3 (M = Li, Na, K as the case may be) was added to the europium-doped samples before the sintering processes. In the subsequent text, blank SrWO₄ will be designated as SWO, europiumdoped SrWO₄ will be designated as SEWO, europium- and lithiumcodoped SrWO₄ as SELWO, europium- and sodium- codoped SrWO₄ as SENWO, and europium- and potassium- codoped SrWO₄ as SEKWO.

2.2. Instrumentation. Powder X-ray diffraction (XRD) measurements were carried out using a Cu K α (λ = 1.5405 Å) monochromatic X-ray source in a Rigaku Miniflex-600 diffractometer. The measurements were carried out in the 2θ range of 10–60° in steps of 0.02° and with a scan rate of 1°/min. SEM images were recorded on a Mini SNE-4500 M Tabletop Scanning Electron Microscope instrument. The EDS or EDX spectrum was recorded on a Bruker Nano GmbH XFlash detector 410-M (Berlin, Germany), and the spectrum was analyzed using Quantax Esprit 2.0 Bruker microanalysis software.

Photoluminescence measurements were carried out on an Edinburgh florescence spectrometer (CD-920 unit). A xenon flash lamp (μ F2, power 150 W, Edinburgh make) was used as the excitation source. Emission spectra were recorded with a step of 1.0 nm/s and a lamp frequency of 100 Hz. Fluorescence lifetime measurements were carried

out using a time-correlated single-photon counting (TCSPC) technique with the frequency of the xenon lamp fixed at 100 Hz.

Positron annihilation lifetime spectroscopy (PALS) measurements were carried with a lifetime spectrometer consisting of two plastic scintillation detectors operated in fast-fast coincidence mode. The time resolution of the spectrometer was 266 ps. The positron source of 15 μ Ci ²²Na, deposited and dried between two 8 μ m polyimide films, was immersed in the powder samples to acquire positron lifetime spectra. Silicon was used as the reference to correct the positron annihilations in the polyimide film used for encapsulating the radioactive source. Doppler broadening of annihilation radiation (DBAR) was measured using an HPGe detector having a time resolution of 2 at 1332 keV γ ray of ⁶⁰Co. The shape (*S*) and wing (*W*) parameters were evaluated from the DBAR spectra as fractional area 511 \pm 0.84 keV, and the *W* parameter was evaluated as fractional wing area in the region of 4.2 \leq $|E_{\gamma} - 511| \leq$ 6.3 keV, where E_{γ} is the energy of γ radiation.

The EXAFS measurements have been carried out at the Energy-Scanning EXAFS beamline (BL-9) at the INDUS-2 Synchrotron Source (2.5 GeV, 200 mA) at Raja Ramanna Centre for Advanced Technology (RRCAT), Indore, India.44,45 This beamline operates in an energy range of 4 to 25 keV. The beamline optics consisted of a Rh/Pt-coated collimating meridional cylindrical mirror, and the collimated beam reflected by the mirror was monochromated by a Si(111) (2d = 6.2709) based double-crystal monochromator (DCM). The second crystal of DCM was a sagittal cylinder used for horizontal focusing while a Rh/Pt coated bendable post mirror facing down was used for vertical focusing of the beam at the sample position. Rejection of the higher harmonics content in the X-ray beam was performed by detuning the second crystal of DCM. In the present case, EXAFS measurements at Eu L3-edges have been performed in fluorescence mode. For measurements in the fluorescence mode, the sample was placed at 45° to the incident X-ray beam and the fluorescence signal $(I_{\rm f})$ was detected using a Si drift detector placed at 90° to the incident X-ray beam. An ionization chamber detector was used prior to the sample to measure the incident X-ray flux (I_0) and the absorbance of the sample ($\mu = I_f/I_0$) was obtained as a function of energy by scanning the monochromator over the specified energy range.

3. RESULTS AND DISCUSSION

3.1. X-ray Diffraction Study: Phase Purity. Powder XRD patterns of undoped, europium-doped, and alkali-metal- and europium-codoped samples of SrWO₄ are shown in Figure 1. The XRD patterns are in agreement with the tetragonal system of SrWO₄ in space group $I4_1/a$ (JCPDS No. 08-0490), and no



Figure 1. Powder X-ray diffraction patterns of Eu^{3+} -doped SrWO₄ samples, codoped with different alkali-metal ions (Li⁺, Na⁺, and K⁺) for charge compensation and the standard diffraction pattern for SrWO₄ (JCPDS No. 08-0490).

additional peaks were detected in doped samples, confirming the phase purity of the samples. Doping of europium and alkali ions (Na⁺ and K⁺) in the samples was confirmed from EDS (energy dispersive X-ray spectroscopy) measurements. The EDS spectrum clearly indicate the efficient doping of europium ion and codoping of Na⁺ and K⁺ ions (Figure S1 inset in the Supporting Information). The peaks due to C are because of the use of carbon tape during the experiment.

3.2. SEM Study. Figure S2 in the Supporting Information shows the SEM micrographs of SWO, SEWO, SENWO, and SEKWO scheelites synthesized using a solid-state route involving intermittent grinding and heating. The sizes of the particles are in the range $3-5 \mu m$, having mostly clustered particles with nondefined facets, which is typical of the solid-state route. Microparticles tend to agglomerate, forming large numbers of small clusters having an irregular morphology, as can also be seen from the micrograph. The variation in size of the clusters is attributed to the inhomogeneous thermal gradient and mass flow in the solid-state reaction.

There are two interesting phenomena which could be seen from the SEM micrographs (Figure S1 in the Supporting Information): microparticles grow in size and the extent of agglomeration also increases as we go from the undoped sample to europium-doped and further to alkali-metal-codoped samples. This may be because of increased lattice strain induced by codoping the larger potassium ion on facets of microparticles.

3.3. X-ray Absorption near Edge Structure (XANES) Spectroscopy: Oxidation State of Europium Ion. Europium has the tendency to become reduced to the +2 oxidation state even in ambient air in some of the hosts. The luminescence properties of Eu^{2+} are driven by f-d transitions whereas those of Eu^{3+} are governed by f-f transitions. The normalized XANES spectra of doped SrWO₄ are shown in Figure 2 along



Figure 2. Normalized XANES spectra of SEWO, SELWO, SENWO, and SEKWO at the Eu L3 edge along with the reference standard Eu_2O_3 .

with the reference spectrum of Eu_2O_3 . The absorption edge position is dependent on the oxidation state of the absorbing atom. The absorption edge position shifts to higher energy with a decrease in oxidation state. XANES spectra of the all the samples are similar to the reference Eu_2O_3 spectrum and exhibit only one maximum at 6978 eV.

The same position of the absorption edge for the entire sample set in comparison to Eu_2O_3 confirms the +3 oxidation state of europium ions in the samples. However, the white line

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peak intensity is quite different for $SrWO_4$ in comparison to Eu_2O_3 . The white line peak intensity depends on the number of unoccupied states present in the system. No significant changes have been observed in edge position; however, small white line peak intensity variation with charge compensator can be seen. The maximum peak intensity is observed for the Li case, and the lowest peak intensity is for the Na case.

3.4. Photoluminescence Spectroscopy: Optical Properties, Site Symmetry, and Colorimetric Performance. Figure 3 depicts the excitation spectrum of alkali-codoped and



Figure 3. Photoluminescence excitation spectra of $SrWO_4:Eu^{3+}$ phosphor codoped with different alkali-metal ions (Li⁺, Na⁺, and K⁺) for charge compensation, at an emission wavelength of 614 nm.

-undoped SrWO4:Eu3+ samples at an emission wavelength of 614 nm corresponding to the ${}^{5}D_{0} - {}^{7}F_{2}$ transition of Eu³⁺. The excitation spectra of $SrWO_4$: Eu^{3+} : M^+ (M = Li, Na, K) have dual features: a broad band in the region 200-300 nm which is attributed to a charge transfer transition from oxygen (O^{2-}) to europium (Eu^{3+}) and fine structures in the region 350–550 nm attributed to an intra-f-f transition of the europium ion. Among these, the most intense is at 395 nm due to a ${}^{7}F_{0}-{}^{5}L_{6}$ transition. This indicates that the synthesized phosphor can be pumped easily using near-ultraviolet light. The codoping of alkalimetal ion induces a change in the intensity of the $O^{2-} \rightarrow Eu^{3+}$ charge transfer band (CTB). Li and K/Na seem to have opposite affects; lithium enhances the CTB intensity, whereas Na/K seems to reduce the intensity. These changes are caused due to changes in Eu-O distances by alkali ion doping, as indicated from EXAFS data (section 3.7). From Table 3 (EXAFS fitted data), it can be seen that lithium incorporation increases the Eu-O bond length from 2.35 to 2.45 Å in SELWO in comparison to SEWO. On the other hand, there are no substantial changes on Na and K codoping. This can be understood in that lithium, being very small in ionic size, can become incorporated at multiple sites in the host lattice very efficiently, which is reflected in its effect on Eu-O bond length enhancement, unlike Na/K ion, which seems to have a negligible effect. Due to the large size of Na/K, they can effectively fit into the lattice sites of only Sr.

Figure 4a shows the emission spectrum of $SrWO_4:Eu^{3+}:M^+$ (M = Li, Na, K) at an excitation of 247 nm corresponding to CTB (host). The emission spectrum at an excitation wavelength of 395 nm corresponding to ${}^7F_0-{}^5L_6$ (f-f transition of Eu^{3+}) is depicted in Figure 4b. The bottom trace in Figure 4a shows the emission profile of undoped $SrWO_4$ (SWO), which consisted of a broad emission around 400-550 nm and is ascribed to oxygen (O²⁻) to tungsten (W⁶⁺) charge transfer.¹⁸ The emission profiles of doped samples (SEWO, SELWO, SENWO and SEKWO) consisted of the typical europium ion spectrum with peaks at 592, 614, 653, and 704 nm. These peaks are attributed to ${}^{5}D_{0} - {}^{7}F_{1}$, ${}^{5}D_{0} - {}^{7}F_{2}$, ${}^{5}D_{0} - {}^{7}F_{3}$, and ${}^{5}D_{0} - {}^{7}F_{4}$ transitions of europium ion. Among these, that at 592 nm $({}^{5}D_{0} - {}^{7}F_{1})$ is called a magnetic dipole transition (MDT, $\Delta I = \pm 1$) and the most intense peak at 614 nm $({}^{5}D_{0}-{}^{7}F_{2})$ is the hypersensitive electric dipole transition (EDT, $\Delta I = \pm 2$). The EDT is highly sensitive to local ligand and crystal field, whereas MDT is insensitive. The MDT is intense when the local environment around europium has inversion symmetry, whereas EDT is highly intense and dominates over MDT if the surroundings around europium lack inversion symmetry. Comparing the relative intensity of MDT and EDT, one can predict the local symmetry around the europium ion. The fact that in all the samples EDT is more intense than MDT is an indication of the fact that the europium environment lacks inversion symmetry and has a distorted environment. The emission spectrum with 247 and 395 nm exhibited similar spectral features, and the only difference is in relative intensity. The emission intensity on excitation with CTB is more than 395 nm, which is because of the fact that f-f transitions are Laporteforbidden in nature. As far as the role of codoping on spectral features is concerned, no noticeable differences are seen.

The local point group symmetry of activator ions in doped phosphors is very important for optimum performance as an optical material. With a very low level of dopant concentration, such structural information is very difficult to decipher from XRD data. However, the emission spectrum of europium ion can give a great deal of information on structural aspects from various ${}^{5}D_{0}-{}^{7}F_{I}$ (J = 1-4) peaks. Moreover, the number of Stark components in these peaks gives information about the point group symmetry of Eu³⁺ in SrWO₄:Eu³⁺ phosphor. Europium ions occupying the Sr²⁺ lattice were used as spectroscopic probes to determine local symmetries of SrO₈ in SrWO₄ scheelite. On the basis of the Stark splitting pattern in the emission spectrum of SrWO₄:Eu³⁺; the point group symmetry of Eu^{3+} was found to be C_6 . This is determined on the basis of the number of Stark components in each of the ${}^{5}D_{0}-{}^{7}F_{I}$ (I = 1-4) peaks.⁴⁶ Spectral patterns of all the emission lines in SrWO₄:Eu³⁺ phosphor are depicted pictorially in Figure 5. The interesting thing is that, in the scheelite structure of SrWO₄, Sr as well as tungsten ion has S_4 site symmetry.⁴⁷ On aliovalent doping by trivalent europium ion, there is lowering in symmetry to C_6 . This is due to charge and size imbalance which invokes the need for charge compensation and distorts the basic SrO₈ network.

The color of any material (whether self-luminous or reflecting) can be easily specified using a point, designated on a color chromaticity figure (known as a color map) through its calculated color coordinates. These color coordinate values are estimated using the corrected emission spectra with the help of $\overline{x}(\lambda)$, $\overline{y}(\lambda)$, and $\overline{z}(\lambda)$, which are called color matching functions and are defined in the CIE 1931 color space for a 2° observer.⁴⁸ It can be very well seen from Figure 6 that the undoped SrWO₄ sample shows bluish green emission under UV excitation. However, on doping with europium ion there is a shift in the color emission from blue-green to the reddish region. This is induced by energy transfer from the host to the dopant ion, which is known as host-sensitized energy transfer. Interestingly SEWO, SENWO, and SEKWO on excitation with CTB as well



Figure 4. Emission spectra of SrWO₄:Eu³⁺ phosphor codoped with different alkali-metal ions (Li⁺, Na⁺, K⁺) for charge compensation at excitation wavelengths of (a) 247 nm and (b) 395 nm.

as 395 nm exhibit similar emission characteristics in terms of colorimetric performance emission in the red region. Samples excited at 247 nm show more of a reddish orange emission, whereas 395 nm samples show more of a reddish pink emission. However, SELWO phosphor shows more consistency and uniform optical performance upon both CTB as well as 395 nm, as it emits in a similar region of the electromagnetic spectrum under both.

3.5. Effect of Alkali Ion Codoping on Optical Performance of Phosphor Materials. 3.5.1. Effect on Photoluminescence Intensity of Red Emitting SrWO₄:Eu³⁺ Phosphor. According to Figure 4, the spectral features (shape, position, etc.) remain the same even on alkali-metal ion codoping. However, it can be very well seen from the same figure that lithium ion incorporation enhances the luminescence output of SEWO phosphor whereas Na and K have opposite effects and reduce the emission output of the europium-doped phosphor sample. This is pictorially represented in Figure 7. In the scheelite structure the local environment around Sr²⁺ is a more distorted site in comparison to W⁶⁺. In SrWO₄, Sr²⁺ is oriented as SrO₈ with S₄ point symmetry whereas W⁶⁺ is coordinated to four oxygen atoms with symmetry similar to that of Sr²⁺ ion. When Eu³⁺ is doped



Figure 5. Transition selective emission profiles of ${}^{5}D_{0}-{}^{7}F_{J}$ (J = 1-4) peaks of europium ion in SrWO₄:Eu³⁺ phosphor.



Figure 6. CIE 1931 chromaticity diagram for undoped, SrWO₄:Eu³⁺, and SrWO₄:Eu³⁺:M⁺ (M = Li, Na, K) phosphor under 247 and 300 nm excitation.

in SrWO₄, considering the closeness in ionic radius, it should become localized at the Sr²⁺ site. However, due to ionic size and ionic charge differences Eu^{3+} doping induces large structural distortion and reduces the symmetry from S_4 to C_6 as discussed in section 3.4. The Kroger–Vink notation for such substitution is

$$2Eu^{\cdots} + 3Sr_{Sr}^{\circ} \leftrightarrow 2Eu_{Sr}^{\circ} + V_{Sr}^{\circ}$$
(1)

As per the current understanding, the negatively charged cation vacancies V_{Sr}^{\cdot} act as sources of nonradiative pathways and successfully quench the luminescence by absorbing the energy from luminescence active europium ion centers.



Emission Intesnity (I_{500-7F2})(a.u.)

Figure 7. Variation of emission output on codoping different charge compensation alkali-metal ions (Li⁺, Na⁺, and K⁺) into SrWO₄:Eu³⁺.

Samples

Eu-Li

Eu-Na

Eu-K

Eu

Generally speaking, vacancies in the host lattice act as luminescent quenching centers.⁴⁹ Introduction of alkali-metal ions increases the emission intensity as they reduce the concentration of V_{Sr}° by compensating for the charge imbalance created by aliovalent substitution of Eu³⁺ at the Sr²⁺ site as well as by reduction in lattice distortion. Most of the literature states that a reduction in cation vacancies is the root cause for luminescence enhancement on alkali codoping.^{23,26–29}

It can be very well seen from the EXAFS calculated (Table 3) Debye–Waller factor (σ^2), which indicates the degree of distortion in Eu-O bonding, indeed decreases on lithium doping whereas it increases substantially with sodium and potassium codoping. A low level of structural distortions in SELWO means fewer structural defects or any kind of charge compensating defects which are sources of nonradiative pathways. Therefore, more emission enhancement could be seen in SELWO in comparison to SENWO/SEKWO. This is the first report of its kind where EXAFS data and PALS perfectly supported the mechanism of luminescence enhancement in europium on lithium codoping and reduction on Na and K codoping in $SrWO_4:Eu^{3+}:M^+$ (M = Li, Na, K) phosphor. Our studies altogether highlighted a different mechanism, where in using PALS it was seen that lithium codoping does not decrease the cation vacancies at all: rather, it sits in the interstices and structurally modifies the SrWO₄ lattice and creates an environment which is conducive for PL enhancement (section 3.6).

Charge compensation is realized by localization of M⁺ ion at an interstitial position which can create M_{Sr} and would give rise to a large concentration of oxygen vacancies V₀. These oxygen vacancies play the role of sensitizers and cause very efficient radiative energy transfer to Eu³⁺ ion due to strong mixing of CTB resulting in enhanced luminescence.⁵⁰ Lattice modification is induced by formation of Eu-O-M types of clusters wherein the local field surrounding the europium ion becomes modulated due to redistribution in electron density around the oxygen ion and therefore more electrons are pulled toward Eu^{3+,51} The enhancement in PL intensity could be seen only for lithium codoping, whereas the incorporation of Na⁺ and K^+ ions into the SrWO₄:Eu³⁺ phosphor leads to a reduction in luminescence intensity (Figure 7). This may be an indication that the addition of the Na^+/K^+ ions introduces the structural defect centers that act as quenching centers of luminescence. Due to its small ionic size, a monovalent lithium ion (0.92 Å) can be easily incorporated into the host lattice either

substitutionally or interstitially in comparison to large Na and K ions (1.18 and 1.51 Å), whereas the eight-coordinated Sr²⁺ has an ionic size of 1.26 Å. This is also seen from large Debye–Waller factor (σ^2) values for SENWO and SEKWO (Table 3), which indicate a large degree of structural distortion on Na and K codoping in SrWO₄:Eu³⁺ phosphor.

3.5.2. Effect on Luminescence Lifetime of Red Emitting $SrWO_4:Eu^{3+}$ Phosphor. The decay profiles are presented in Figure 8 with excitation of 247 nm; corresponding individual



Figure 8. Luminescence lifetime decay profile of $SrWO_4:Eu^{3+}$ phosphor codoped with different charge compensation alkali-metal ions (Li⁺, Na⁺, and K⁺) at an excitation wavelength of 247 nm.

and average lifetime values are presented in Table 1. The time taken by each component to decay was extracted by fitting the

Table 1. Lifetime Values of SrWO₄:Eu³⁺ Phosphor Codoped with Different Charge Compensation Alkali-Metal Ions (Li⁺, Na⁺, and K⁺) at an Excitation Wavelength of 247 nm

	$\lambda_{\rm ex}$ 24	7 nm		
sample	$ au_1$ (μ s)	$\tau_2 \ (\mu s)$	$ au_{\mathrm{av}} \ (\mu \mathrm{s})$	asymmetry ratio $({}^{5}D_{0}-{}^{7}F_{2}/{}^{5}D_{0}-{}^{7}F_{1})$
SEWO	407 (28%)	734 (72%)	642	9.61
SELWO	311 (28%)	693 (72%)	588	9.52
SENWO	514 (60%)	886 (40%)	663	9.10
SEKWO	351 (80%)	662 (20%)	600	9.19

decay profile using the second-order decaying exponential curve (eq 1):

$$I(t) = A \exp(-t/\tau_1) + B \exp(-t/\tau_2)$$
(2)

where *I* is the luminescence intensity, *A* and *B* are residual weighting factors, *t* is the time of measurement, and τ_1 and τ_2 are the decay times of the first and second components, respectively.

The luminescence decay profile seems to have two lifetime components, namely the fast and the slow components which correspond to the lifetime coming from Eu³⁺ emission near and far from the charge-compensating defects (cation vacancies in this case), respectively, which arises due to aliovalent substitution of europium ion at strontium sites. The longer-lived species ($T_{\rm L} = 662-886 \ \mu s$) is attributed to europium ion occupying regular SrO₈ polyhedra which are far from cation vacancies. The other lifetime (shorter one) is attributed to

europium ion occupying SrO₈ but very near to charge compensation defects ($T_{\rm S}$ = 311–514 μ s).

An interesting thing which could be seen from Table 1 is that for SEWO and SELWO the population of short-lived component (T_{s} , 28%) is less than that of the long-lived component $(T_1, 72\%)$. This indicates that for both of these samples a greater percentage of europium ions (Eusr) are far from chargecompensating defects. On the other hand, for SENWO and SEKWO the population of short-lived species (T_{s_i} 60 and 80%) for Na and K) is greater than that of long-lived species $(T_{s},$ 40 and 20% for Na and K). This highlights that for Na- and K-codoped samples the percentage of europium is more in the vicinity of charge-compensating defects. It can be seen from Table 1 that the average lifetime value also changes on alkali codoping. Interestingly the sodium ion codoped sample (SENWO) was found to have the maximum luminescence lifetime. This is correlated with asymmetry ratio value, which is the ratio of ${}^{5}D_{0} - {}^{7}F_{2}$ to ${}^{5}D_{0} - {}^{7}F_{1}$, which is also shown in Table 1. Invariably it could be seen from Table 1 that the asymmetry ratio decreases on alkali doping but the decrease was found to be maximum for SENWO and minimum for SELWO, which is directly reflected in their highest and lowest average lifetime values, respectively. The lowest asymmetry ratio for SENWO samples indicated a relatively less asymmetric environment around europium in comparison to other samples. Therefore, Laporte's selection rules are more forbidden in comparison to other samples, which means higher lifetime values.

3.6. Judd-Ofelt Analysis. Judd-Ofelt analysis is a very powerful tool to calculate the transition probability of electric dipole transitions.^{52,53} Radiative and nonradiative transition rates, branching ratios, quantum efficiences and Judd-Ofelt parameters are very useful in designing phosphor materials for commercial applications. The detailed methods of calculation are reported in our earlier work.⁵⁴ The Judd-Ofelt parameters Ω_2 and Ω_4 are highly informative and give ideas about the local symmetry, covalency, and polarizability around the Eu-O bond. Radiative transition rates were calculated for the samples, and it was found to be maximum for SELWO and minimum for SEKWO with respect to SEWO. In fact, Na/K codoping decreases the radiative transition probability of red emitting SrWO₄:Eu³⁺ phosphor. The same reason also fits well here, which was used to justify the enhancement in emission intensity. In terms of quantum yield there is not much improvement on alkali codoping, although the SEKWO sample still has the worst performance, which is justifiable due to its very low radiative transition rate, as it induces the maximum lattice distortion as also indicated by the Debye-Waller factor calculated using EXAFS measurements. In all of the samples Ω_2 was found to be greater than Ω_4 , which indicated low symmetry and high covalency around the Eu-O bond. All of the photophysical properties and Judd-Ofelt parameters are given in Table 2.

3.7. Positron Annihilation Spectroscopy. The positron annihilation characteristics in the material carry the signature of the nature of the defects in the samples. The positron annihilation lifetime spectra of all samples were analyzed using the computer program PALSfit,⁵⁵ which fits the spectra as multi-exponential decay convoluted with the time resolution of the positron lifetime spectrometer.

All the spectra fitted well to two lifetime components. The second lifetime component is in the range of 1 ns and <2% in intensity. The positronium-like component in oxide powders has been well reported and is attributed to the positron annihilations in the intergranular spaces in the powder samples^{56–58}

Table 2. Luminescence Lifetimes,	Radiative and Nonradiati	ve Decay Rates, Quantum	ا Efficiencies (°D ₀ Level)	, and Judd–Ofelt
Intensity Parameters for SrWO ₄ :Eu	³⁺ Phosphor Codoped with	1 Different Charge Compe	nsation Alkali Metal Ions	$(Li^+, Na^+, and K^+)$





Figure 9. (a) Positron annihilation lifetimes in europium-doped SrWO₄ samples codoped with different alkali ions for charge compensation. (b) S-W plot from Doppler broadening of annihilation radiation measurements.

and is not discussed further. The first component in all samples is in the range of 220-240 ps. An additional intermediate component in the range of 400-600 ps has been observed in different nanoparticles, including that of SrWO₄,¹⁸ and is attributed to the positron annihilations from the surface of the nanoparticles. The crystallite size in the present case is much larger, as indicated by the sharp XRD pattern, and the positron diffusion to the surface of the nanoparticles is negligible. In the cases where this intermediate component is very small, the first lifetime component and only average lifetime are extracted from the spectra. The positron lifetime in the undoped SrWO₄ is 221.4 \pm 0.8 ps. A single lifetime component is obtained in the cases of defect-free single crystals or saturated trapping of positrons in the defects. Even in the case of disordered materials with shallow positron traps, the trapped positron lifetime might be difficult to determine and only one component which is longer than the bulk lifetime component but shorter than the lifetime for annihilations from saturated trapping in defects is obtained.⁵⁹ The average lifetimes in this range are observed in perovskites where vacancies in both A and B sites coexist.⁶⁰ In the current case, this is more likely, as positron lifetimes in the range of more than 200 ps are not observed due to positron annihilations in bulk and oxide samples as in the current case are seldom defect free.

The lifetimes in all the samples are shown together in Figure 9a. On europium doping the positron lifetime increases to 230 ps. The increase in the positron lifetime can be caused by an increased concentration ratio of vacancies in the Sr to W lattice. Substitution of two Eu^{3+} ions in place of three Sr^{2+} ions for charge compensation is expected to enhance Sr vacancies, and substitution of Eu^{3+} in the W lattice is not expected due to size differences. In addition to cation vacancies, interstitial oxygen

could also be a path of charge compensation operating in these materials. Alkali ions are codoped with europium for compensation and account for the supposed cation vacancies that are created by substitution of Eu^{3+} in place of Sr^{2+} . Codoping of K with europium resulted in positron lifetimes nearly the same as those of undoped SrWO₄, suggesting that the addition of K reduces the additional formation of the vacancies in the Sr lattice. When the codoped ion is Na, the positron lifetime is intermediate between the undoped and europium-doped samples, showing partial charge compensation only. The differences in charge compensation by Na/K codoping might be due to their large ionic size in comparison to lithium ion. Codoping with Li⁺ has increased the positron lifetime of the europium-doped samples, suggesting that Li⁺ doping does not decrease the cation vacancy concentration. The enhanced lifetime indicates that Li might be occupying interstitial sites rather than lattice positions due to its very small size and further contribution to oxygen vacancies.

To see the differences between the nature of the defects in these samples, shape (S) and wing (W) parameters have been evaluated from the DBAR spectra. The S-W correlation plot of these samples is shown in Figure 9b. S-W values of the samples having a similar nature of defects but differing in their concentrations fall on a straight line with samples with higher vacancy concentrations falling in the higher S parameter range. It is seen from the figure that S-W values of all samples except the Li⁺codoped sample fall on a straight line with undoped and only europium doped samples at the extremes. The plot also shows that codoping of Na⁺ and K⁺ contributes to an effective decrease in the cation vacancy concentrations, while Li⁺ doping does not show a similar trend. Further structural changes arising due to alkali codopants have been investigated by EXAFS.



Figure 10. Normalized EXAFS spectra of SEWO, SELWO, SENWO, and SEKWO at Eu L3 edge.

3.8. EXAFS Spectroscopy. Figure 10 shows the normalized EXAFS spectra of SrWO₄:Eu³⁺. In order to take care of the oscillations in the absorption spectra, $\mu(E)$ has been converted to absorption function $\chi(E)$, defined as⁶¹

$$\chi(E) = \frac{\mu(E) - \mu_0(E)}{\Delta \mu_0(E_0)}$$
(3)

where E_0 is absorption edge energy, $\mu_0(E_0)$ is the bare atom background, and $\Delta \mu_0(E_0)$ is the step in $\mu(E)$ value at the absorption edge. The energy-dependent absorption coefficient $\chi(E)$ has been converted to the wavenumber-dependent absorption coefficient $\chi(k)$ using the relation

$$K = \sqrt{\frac{2m(E - E_0)}{\hbar^2}} \tag{4}$$

where *m* is the electron mass. $\chi(k)$ is weighted by k^3 to amplify the oscillation at high *k*, and the $\chi(k)k^3$ functions are Fourier transformed in *R* space to generate the $\chi(R)$ versus *R* spectra in terms of the real distances from the center of the absorbing atom. The set of EXAFS data analysis programs available within the IFEFFIT software package have been used for EXAFS data analysis.⁶² This includes background reduction and Fourier transform to derive the $\chi(R)$ versus *R* spectra from the absorption spectra (using ATHENA software), generation of the theoretical EXAFS spectra starting from an assumed crystallographic structure, and finally fitting of experimental data with the theoretical spectra using ARTEMIS software.

The $\chi(R)$ versus R plots generated (Fourier transformed range k = 2.0-10.0 Å⁻¹) for all of the samples from the $\mu(E)$ versus E spectra following the methodology described above are shown for SrWO₄:Eu³⁺ measured at the Eu L3 edge in Figure 11. The structural parameters (atomic coordination and lattice parameters) of SrWO₄ used for simulation of theoretical EXAFS spectra of the samples have been obtained from ref 63, and the best fit $\chi(R)$ versus R plots of the samples have been shown in Figure 11 along with the experimental data for all the samples. The bond distances and disorder (Debye–Waller) factors (σ^2), which give the mean-square fluctuations in the distances, have been used as fitting parameters. The best-fit results of the above are summarized in Table 3. The first peak of SrWO₄:Eu³⁺ (Figure 11a) is the contribution of eight oxygen



Figure 11. Fourier-transformed EXAFS spectra of $SrWO_4:Eu^{3+}:M^+$ (M = Li, Na, K) phosphors at Eu L3-edge (scatter points) and theoretical fits (solid lines) for (a) SEWO, (b) SELWO, (c) SENWO, and (d) SEKWO.

atoms at a bond distance of 2.35 Å. The plots shown in Figure 11 are phase-uncorrected spectra which show peaks with slightly shorter bond distance than the actual distance; however, the fitting results obtained here are phase corrected. The first Eu-O bond distance is increased for the Li case to 2.45 Å; however, it is again decreased for the Na and K case. The σ^2 value, which gives the mean-square fluctuations in the bond distances, increases as we go from Li to Na and Na to K. It can be observed clearly that the distance of the second coordination peak (at 3.0 Å in Figure 11a) is shifted to lower bond distance for the Na and K case in comparison to the Li case. These results clearly explain why Li⁺ enhances the emission intensity whereas Na⁺ and K⁺ degrade it. This is explained in terms of Debye–Waller factor (σ^2), which is the indirect parameter related to degree of distortion. The Debye-Waller factor decreases on lithium codoping, whereas it increases substantially on Na⁺ and K⁺ codoping. This is attributed to the small ionic size of lithium ion. In addition, EXAFS data successfully explained the variation in intensity of CTB on Li/Na/K codoping. Lithium enhances the CTB intensity, whereas Na/K seems to reduce the intensit,y which is explained in terms of Eu–O bond length variation on Li/Na/K codoping.

4. CONCLUSION

In contrast to conventional explanations where removal of erstwhile created cation vacancies during lanthanide doping by alkali codopants are the prime reason for PL enhancements, the present studies showed opposite trends. Na^+/K^+ codoping, where V_{sr} concentration (PALS) is reduced, showed lower PL efficiency than Li-doped samples, where the V_{sr} concentration did not decrease. Due to the larger size of K^+ and Na^+ , they can efficiently fit only Sr^{2+} lattice sites, while Li⁺ being a smaller ion can occupy Sr^{2+} , W^{6+} , or interstices. This resulted in reduced vacancy concentrations in Na^+ - and K^+ -doped samples.

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path	param	SEWO	SELWO	SENWO	SEKWO
Eu-O	R (Å)	2.35 ± 0.01	2.45 ± 0.01	2.34 ± 0.01	2.37 ± 0.01
	N	8	8	8	8
	σ^2 (Å ²)	0.0016 ± 0.0006	0.0012 ± 0.0009	0.0059 ± 0.0008	0.0068 ± 0.001
Eu-W	R (Å)	3.79 ± 0.01	4.27 ± 0.01	3.66 ± 0.01	3.43 ± 0.01
	N	4	4	4	4
	σ^2 (Å ²)	0.0012 ± 0.0006	0.0012 ± 0.0007	0.0015 ± 0.001	0.0034 ± 0.001

Table 3. Bond Lengths, Coordination Numbers, and Disorder Factors Obtained by EXAFS Fitting for $SrWO_4:Eu^{3+}:M^+$ (M = Li, Na, K) Phosphors

However, removal of vacancies also results in less asymmetry around Eu³⁺ and lower PL. In Li⁺ doping, the greater positron lifetime in comparison to that of the non-alkali-doped sample suggests reduced distortions in the lattice that may be the result of Li⁺ occupying interstices. This is also expected to increase oxygen vacancies and reduce structural defects that are known to enhance PL emission. Li doping also resulted in greaater Eu-O bond lengths in comparison to Na⁺/K⁺ doping. The asymmetry around Eu³⁺ also was reduced in Na⁺/K⁺ doping, as shown by lower ${}^{5}D_{0} - {}^{7}F_{2} / {}^{5}D_{0} - {}^{7}F_{1}$ emission intensities and higher Debye-Waller factors. The former reduces radiative transitions, while the latter enhances nonradiative transitions. This seems to be the reason for a decrease in PL in Na⁺/K⁺doped samples. Rather than cation vacancy concentrations, the structural changes around the Eu³⁺ ion seem to be deterministic factors in the PL properties of alkali-codoped SrWO₄:Eu samples.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.7b02780.

SEM micrographs of SrWO₄, SrWO₄:Eu³⁺, SrWO₄:Eu³⁺: Na⁺, and SrWO₄:Eu³⁺:K⁺ and their corresponding EDS spectra (PDF)

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ACKNOWLEDGMENTS

The authors thank Mr. Rohan Phatak (Fuel Chemistry Division, BARC) for XRD measurements.

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