# Facile Chemical Insertion of Lithium in $Eu_{0.33}Zr_2(PO_4)_3$—An Elegant Approach for Tuning the Photoluminescence Properties

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Solid state lighting (SSL) technology using light emitting diodes (SSL-LED) is an important tool for energy saving by replacing the conventional incandescent and fluorescent lamps. However, one of the key issues in SSL-LED technology is to improve color rendering index (CRI). The commercial phosphor (YAG:$Ce^{3+}$) used for white light generation has disadvantages of low CRI due to the lack of emission in the red region.[1] Recently, different classes of compounds (nitrides, oxy-nitrides, and halides) activated by $Eu^{2+}$ and $Ce^{3+}$ are considered to be possible candidates for SSL application.[2−6] Since the outer 5d orbitals are involved in optical transitions in the case of $Eu^{2+}$ and $Ce^{3+}$ ($4f^{n-1}5d^1 \rightarrow 4f^n$), the emission line widths from these activators are broad and are typically 30−80 nm. The human eye visual perception is maximum at 550 nm, and hence, for good CRI, the emission line width should be lower in the red region.[7] Among all the rare earths, Eu is a well-known activator. Both $Eu^{2+}$ and $Eu^{3+}$ find enormous applications in the field of phosphors. $Eu^{2+}$ is a broadband emitter with emission in the blue-green region. The emission wavelength of $Eu^{2+}$ can be tuned since the f−d optical transitions involved depend on the crystal field effects imposed by the host lattice. On the other hand, $Eu^{3+}$ is a narrow band emitter with orange to red emission: 580 ($^5D_0 \rightarrow {}^7F_0$), 590 ($^5D_0 \rightarrow {}^7F_1$), and 615 nm ($^5D_0 \rightarrow {}^7F_2$), and the emission color depends on the intensity ratio of these three transitions, which is strongly dependent on the site symmetry of the crystal lattice.[8] Hence, combining the two activators in a single host lattice, $Eu^{3+}$ and $Eu^{2+}$, should be a possibility to generate white light with superior color coordinates. However, to orchestrate the coexistence of these two activators in a single host lattice is a daunting task. In this respect, the Eu(III) containing phosphate, $Eu_{0.33}Zr_2(PO_4)_3$,[9] which belongs to the family of $NaZr_2(PO_4)_3$ (NZP) compounds,[10] is of great interest. The NZP structure with its rigid open framework offers two types of sites for various cations to occupy, type I with 6-fold coordination and type II with 8-fold coordination. In this structure, the type I and type II are partially filled with vacant sites available for the guest cations to occupy. Insertion of lithium in these vacant sites is studied in several NZP type phases.[11,12] In $Eu_{0.33}Zr_2(PO_4)_3$, only one-third of the type I sites are filled by $Eu^{3+}$. This offers the possibility to insert Li in the vacant sites and thereby synthesize phases containing $Eu^{2+}$ and $Eu^{3+}$ species, in the same structure. In the present study, we report on the synthesis of a mixed valent $Li_xEu^{II}_xEu^{III}_{0.33-x}Zr_2(PO_4)_3$ with the NZP structure, using soft chemistry. We compare the luminescence emission properties of $Eu^{3+}$/$Eu^{2+}$ containing phase with the isotypic Eu(II) phase $Eu_{0.5}Zr_2(PO_4)_3$.[13] We show that the lithiated phosphate exhibits blue-white and red-white emission under 393 and 463 nm excitation wavelengths, respectively, as a result of the combination of blue-green emission from $Eu^{2+}$ and red emission from $Eu^{3+}$. The calculated chromaticity coordinates (CIE) are shifted from the red region for the parent phase toward the white region upon Li insertion.

The synthesis of $Eu^{III}_{0.33}Zr_2(PO_4)_3$ has been carried out by the gel route.[9] Stoichiometric amounts of starting materials $Eu_2O_3$ (Alfa Aesar; 99.9%) and $ZrOCl_2 \cdot 8H_2O$ (Alfa Aesar; 99.9%) were dissolved in 2 N $HNO_3$; addition of $NH_4H_2PO_4$ (Prolabo; AR grade) to the metal nitrate solution under constant stirring resulted in a colorless gel. The obtained gel was dried at 75 °C/24 h and progressively heat treated to various temperatures 300 °C/24 h, 800 °C/24 h in air. For the synthesis of $Eu^{II}_{0.5}Zr_2(PO_4)_3$ the final heat treatment was performed under mild reducing atmosphere at 800 °C/24 h for the reduction of $Eu^{3+}$ to $Eu^{2+}$.

Electrochemical lithium insertion studies were carried out by using Swagelok type cells with lithium metal as the negative electrode. The composite positive electrode was prepared by mixing 80 wt % active material with 20 wt % acetylene black. The mixture was pressed onto a stainless steel plate to form the electrode. Chemical lithiation was carried out using $Bu^nLi$ (Alfa Aesar; 2.5 M in hexane) in an argon filled glovebox. Finely ground powder of the parent phase is taken in a conical flask, and an excess amount $Bu^nLi$ solution was added. The contents of the flask were kept under constant stirring. The compounds were recovered by cen-

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**Table 1. Concentration of Li in Chemically Reduced Samples at Different Conditions**

| Temperature | Duration of reaction (days) | No. of Li per formula unit |
|---|---|---|
| RT (20 °C) | 1 | 0.06 |
| RT (20 °C) | 3 | 0.08 |
| 50 °C | 1 | 0.08 |
| 50 °C | 3 | 0.10 |

trifugation, repeatedly washed with hexane, and dried in the glovebox at room temperature (RT).

A Philips X'pert diffractometer was used for phase identification. The diffraction patterns of Li inserted samples were recorded under running vacuum. The profile refinement of parent and Li inserted phases was carried out using the FULLPROF refinement program.[14] ESR spectra were recorded by Bruker EMX-220 X-band ($\upsilon = 9.47$ GHz) spectrometer. The photoluminescence excitation and emission spectra were recorded using a Horiba Jobin Yvon Fluorolog-3 spectrofluorometer having 450 W xenon lamp source with operating range from 220 to 850 nm. CIE coordinates were calculated from the fluorescence emission spectra.[15] The concentration of Li in the lithiated samples was estimated by atomic absorption spectrometric analysis (SpectrA A20, Varian, Australia). For this purpose, a few milligrams of the sample were dissolved in hot aqua regia and filtered to remove any undissolved particles, and the solution was subjected to the analysis.

To ascertain the possibility of reduction of $Eu^{3+}$ to $Eu^{2+}$ through Li insertion in the NZP strcture, the electrochemical insertion of Li in $Eu^{III}_{0.33}Zr_2(PO_4)_3$ was carried out at RT at C/300 rate (insertion of one Li in 300 h). The voltage composition $V(x)$ curve shows that [Supporting Information] insertion of approximately 0.2 Li per formula unit takes place in the voltage window 2−1 V. It is expected that the insertion process is accompanied by reduction of $Eu^{3+}$. To establish the presence of $Eu^{2+}$ in the lithiated phase, we have carried out photoluminescence (PL) and ESR studies. As a result of the electronically insulating nature of $Eu^{III}_{0.33}Zr_2(PO_4)_3$, addition of conducting carbon was necessitated for carrying out the electrochemical reaction. The material, mixed with carbon, is unsuitable for PL studies. We, therefore, attempted chemical insertion using *n*-butyllithium. It is known that the potential of $Bu^nLi$ vs $Li/Li^+$ is approximately equivalent to 1 V,[16] which corresponds to the lower limit of the voltage window chosen for the electrochemical insertion. To improve the kinetics and facilitate the insertion process, the reaction was carried out at elevated temperature (50 °C) for 3 days. The Li content in the inserted phases is estimated by AAS, and the results on Li inserted phases wherein the chemical insertion was carried out under different reaction conditions are summarized in Table 1. A maximum of 0.1 Li could be inserted corresponding to the nominal formula $Li_{0.1}Eu^{II}_{0.1}Eu^{III}_{0.23}Zr_2(PO_4)_3$.

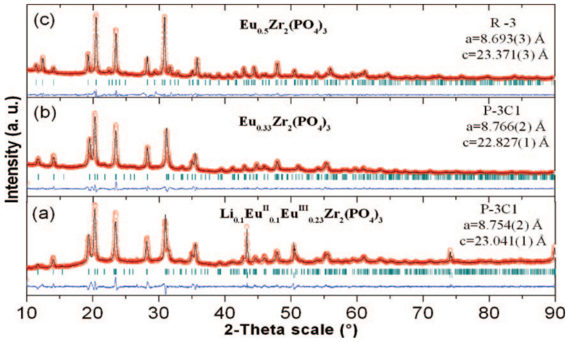

**Figure 1.** Rietveld refinement plot of powder XRD data for (a) $Li_{0.1}Eu^{II}_{0.1}Eu^{III}_{0.23}Zr_2(PO_4)_3$, (b) $Eu_{0.33}Zr_2(PO_4)_3$, and (c) $Eu_{0.5}Zr_2(PO_4)_3$.

**Table 2. Crystallographic Data**

| Structural parameters | $Eu^{III}_{0.33}Zr_2(PO_4)_3$ | $Li_{0.1}Eu^{II}_{0.1}Eu^{III}_{0.23}Zr_2(PO_4)_3$ | $Eu^{II}_{0.5}Zr_2(PO_4)_3$ |
|---|---|---|---|
| space group | $P\bar{3}C1$ | $P\bar{3}C1$ | $R\bar{3}$ |
| *a* (Å) | 8.766(2) | 8.754(2) | 8.693(3) |
| *b* (Å) | 8.766(2) | 8.754(2) | 8.693(3) |
| *c* (Å) | 22.827(1) | 23.041(1) | 23.371(3) |
| cell volume ($Å^3$) | 1514.26(2) | 1529.35(6) | 1529.78(4) |
| $\chi^2$ (%) | 1.80 | 2.70 | 3.96 |
| $R_b$ (%) | 3.21 | 1.05 | 1.45 |
| $R_f$ (%) | 1.92 | 0.899 | 1.59 |

The XRD pattern of the lithiated phase $Li_{0.1}Eu^{II}_{0.1}Eu^{III}_{0.23}Zr_2(PO_4)_3$ is similar to that of the parent phase $Eu^{III}_{0.33}Zr_2(PO_4)_3$. The parent phase crystallizes in the space group $P\bar{3}C1$,[17] wherein one-third of the type I sites are filled. On the other hand, in $Eu_{0.5}Zr_2(PO_4)_3$, half of the type I sites are occupied and the phase crystallizes with the space group $R\bar{3}$.[13] Rietveld refinement of the presently synthesized lithiated phase can be best fitted with the space group $P\bar{3}C1$ (Figure 1). In the lithiated phase, the "*a*" parameter decreases and the "*c*" parameter increases vis-à-vis the parent phase. Such anisotropic behavior is reminiscent of phases with $P\bar{3}C1$ space group.[17] The refined agreement factors and the lattice parameters are given in Table 2.

The ESR spectrum of $Li_{0.1}Eu^{II}_{0.1}Eu^{III}_{0.23}Zr_2(PO_4)_3$ was recorded at RT for a 9.81 GHz frequency to establish the presence of $Eu^{2+}$ [Supporting Information]. As a result of the $4f^7$ electronic configuration and electron spin $S = 7/2$, $Eu^{2+}$ exhibits, generally, a fine structure in the ESR spectrum[18] consisting of seven lines resulting from the transitions between different $m_j$ levels ($7/2 \rightarrow -7/2$). However, in the present case a broad signal centered at 3445 G is observed devoid of the fine structure. The broadness is probably because the spectrum is recorded at RT. Also, since $Eu^{2+}$ ions are present in sites with low symmetry (distorted octahedra) the fine structure is not discernible. Both the factors, namely, the broadness of the peak and the presence of $Eu^{2+}$ in a low symmetry site, contribute to the absence of fine structure in the spectrum. The calculated value of the *g* parameter is 2.034 in good agreement with the value reported for $Eu^{2+}$.[19]

The reduction of $Eu^{3+}$ to $Eu^{2+}$ upon Li insertion is further confirmed by recording the PL spectra of parent and Li

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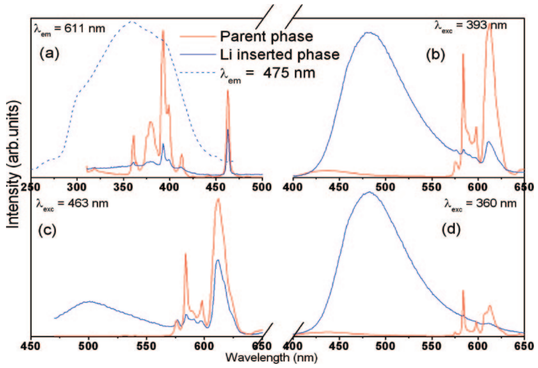

**Figure 2.** PL spectra of chemically reduced sample $Li_{0.1}Eu^{II}_{0.1}Eu^{III}_{0.23}Zr_2(PO_4)_3$ and that of the parent $Eu_{0.33}Zr_2(PO_4)_3$: (a) excitation spectra, $\lambda_{em}$ = 611 nm, and emission spectra under 393 nm (b), 463 nm (c), and 360 nm (d).

inserted phases. The PL excitation and emission spectra of the parent and Li inserted phases at different excitation and emission wavelengths are shown in Figure 2. The parent phase shows characteristic $Eu^{3+}$ PL spectra, and the observed excitation and emission lines are in good agreement with the literature report.[9] The presence of the unique emission line at 576 nm ($^5D_0 \rightarrow {}^7F_0$) indicates that $Eu^{3+}$ occupies only one site in the lattice. The presence of both electric ($^5D_0 \rightarrow {}^7F_2$) and magnetic dipole ($^5D_0 \rightarrow {}^7F_1$) transitions in the emission spectrum confirms that the site occupied by $Eu^{3+}$ is not strictly centrosymmetric. It is known that $Eu^{3+}$ occupies distorted octahedral sites (type I) in NZP structure. The PL spectrum of the reduced phase shows signature of both $Eu^{3+}$ and $Eu^{2+}$ excitation and emission bands. The emission spectra consist of a broadband peaking at 465 nm corresponding to $Eu^{2+}$ and a series of emission lines in the range 570−650 nm corresponding to $Eu^{3+}$. From Figure 2c,b it is evident that both the excitation wavelengths, namely, $\lambda_{exc}$ = 393 and 463 nm, give rise to emission in the blue-green as well as red regions. The emission properties of $Eu^{2+}$ in the reduced phase are compared with those of the $Eu^{2+}$ containing phase, $Eu_{0.5}Zr_2(PO_4)_3$, synthesized in the present study [Figure 3]. The broad emission band at 465 nm matches well with the $Eu^{2+}$ emission band in the chemically reduced sample. This confirms that the observed broad emission band in the emission spectrum of the reduced sample is due to the presence of $Eu^{2+}$. Fine tuning of the emission properties of $Eu^{3+}$ and $Eu^{2+}$ is possible by varying the concentration of Li in the host lattice, thereby varying the $Eu^{3+}/Eu^{2+}$ ratio. From Table 1 it is clear that the concentration of $Li^+/Eu^{2+}$ in the reduced phase increases with reaction time and temperature. The CIE coordinates, calculated from PL spectra of parent and reduced phases, are given Table 3.

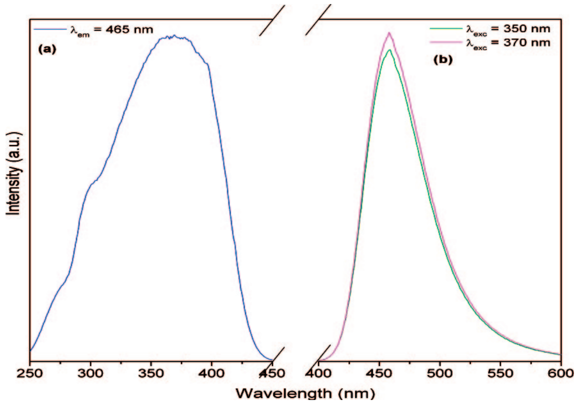

**Figure 3.** PL excitation and emission spectra of $Eu_{0.5}Zr_2(PO_4)_3$.

**Table 3. Calculated Chromaticity Coordinates of the Parent and Lithiated Phase at $\lambda_{exc}$ = 393 nm**

| | | Chromaticity coordinates | |
|---|---|---|---|
| Composition | Reaction conditions | *x* | *y* |
| $Eu_{0.33}Zr_2(PO_4)_3$ | | 0.5950 | 0.3258 |
| $Li_{0.06}Eu^{II}_{0.06}Eu^{III}_{0.27}Zr_2(PO_4)_3$ | RT/1 d | 0.2860 | 0.4586 |
| $Li_{0.08}Eu^{II}_{0.08}Eu^{III}_{0.25}Zr_2(PO_4)_3$ | RT/3 d | 0.2460 | 0.3931 |
| $Li_{0.08}Eu^{II}_{0.08}Eu^{III}_{0.25}Zr_2(PO_4)_3$ | 50 °C/1 d | 0.2551 | 0.4031 |
| $Li_{0.1}Eu^{II}_{0.1}Eu^{III}_{0.23}Zr_2(PO_4)_3$ | 50 °C/3 d | 0.2443<br>(0.3945) | 0.3276<br>(0.1525)[a] |

[a] $\lambda_{exc}$ = 463 nm.

The CIE coordinates are significantly changed upon Li insertion and shift towards the white region as the concentration of Li increases in the host. The reduced phase with the composition $Li_{0.1}Eu^{II}_{0.1}Eu^{III}_{0.23}Zr_2(PO_4)_3$ has reasonable CIE coordinates and shows white emission under UV lamp due to the mixing of both $Eu^{2+}$ (blue green) and $Eu^{3+}$ (red) emission bands.

In conclusion, the possibility of reduction of $Eu^{3+}$ to $Eu^{2+}$ at RT in the NZP structure, using the soft chemistry route, is demonstrated for the first time. These studies open new vistas to the exploration of many other compounds characterized by an open framework and containing trivalent europium. The potential for the synthesis of mixed valent $Eu^{3+}/Eu^{2+}$ compounds, by way of lithium insertion, is demonstrated. Such a method is of significant interest for the realization and optimization of photoluminescent materials, since it allows tuning the $Eu^{3+}/Eu^{2+}$ ratio by controlling the lithium content in the lattice and thereby enables achieving the ideal white light emission required in SSL-LED applications.

**Supporting Information Available:** Electrochemcial Li insertion in $Eu_{0.33}Zr_2(PO_4)_3$ and ESR spectrum of $Li_{0.1}Eu^{II}_{0.1}Eu^{III}_{0.23}Zr_2(PO_4)_3$ at RT. This information is available free of charge via the Internet at http://pubs.acs.org.

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