Luminesce Study on the Impact of Alkaline Earth Metal Ions on Na_3PO_4:Ce^{3+} Phosphors for Colour Display Applications.

Amanda Sefage, Machaba Letswalo, and Buyi Sondezi

Department of Physics1, University of Johannesburg, Auckland Park, 2005, Johannesburg, South Africa

E-mail: asefage@uj.ac.za

Abstract. This study explores the impact of metal ions (Ca, Sr, and Ba) on the optical properties of Na_3PO_4. The resulting nanophosphors, $NaCaPO_4$, $NaSrPO_4$, and $NaBaPO_4$, were synthesized via solid-state reaction techniques and doped with 1 mol% Ce^{3+} The synthesized nanophosphors were annealed at 900°C for 4 hours. A combination of characterization techniques, including XRD, FE-SEM, and PL spectroscopy, were employed to comprehensively characterize the phosphor materials. Additionally, Commission Internationale de l'Eclairage (CIE) plots were generated from the PL data to evaluate and compare the color tuning properties of each phosphor material. XRD analysis revealed that $NaSrPO_4$ phosphors adopted a monoclinic phase structure, whereas Na_3PO_4, $NaCaPO_4$, and $NaBaPO_4$ phosphors crystallized into an orthorhombic phase structure. Notably, doping with 1 mol% Ce^{3+} did not alter the crystal structure phases of these phosphor materials. However, according to the CIE diagram it is observed from the PL emission spectra that the introduction of Ce^{3+} ions and the metal ions on the Na_3PO_4 host phosphors had an impact on the luminescent properties of these materials which suggest it to be good for LEDs with emissions from blue to violet region, as shown in the CIE diagram.

1 Introduction

This study explores the impact of metal ions (M = Ca, Sr, and Ba) on the luminescent properties of Na_3PO_4 (tetragonal, $P\bar{4}21c$) [1], and $NaMPO_4$ nano-phosphor materials. However, the focus is on the application of these nanophosphors for colour display devices results from the variation of the M atoms and additionally replacing these atoms with the rare-earth Ce^{3+} ions for optimum violet-colour emissions using the solid-state reaction method. Rare earth-doped alkaline metal phosphates phosphors have been showing interest in the development and investigation of new efficient luminescent materials due to their remarkable luminescent behaviours based on their structural properties (orthophosphate). Luminescence properties of rare earth ions in various host materials are affected by the crystal structure, phase transition and chemical surroundings [2]. Ce^{3+} is also sensitive to the crystal field environment. This study will demonstrate the application of the solid-state reaction method to synthesize and incorporate alkaline metal ions into the host lattice matrix, followed by the single doping of the resultant compound with Ce^{3+} ions, yielding final mixtures of $NaBaPO_4$:xCe^{3+}, $NaCaPO_4$:Ce^{3+}, and $NaSrPO_4$:Ce^{3+} as phosphors for the investigation of high-intensity blue to violet color emissions. Photoluminescence results indicate improved violet color emissions generated by the $NaMPO_4$:xCe^{3+} phosphor materials. These findings suggest that the synthesized materials may serve as attractive options for color display systems.

2 Experimental

2.1 *Synthesis technique*

The solid-state synthesis method was used to create a series of Ce^{3+} doped sodium phosphates (Na_3PO_4) together with the introduction of alkaline metal ions into the host lattice of Na_3PO_4 to form an orthophosphate, mixture ($NaMPO_4$). To create a uniform powder, the stoichiometric amounts of Na_3PO_4, $NaBaPO_4$, $NaCaPO_4$, and $NaSrPO_4$ for each series were weighed and ground for 30 minutes with an agate mortar and pestle with the use of acetone as a wetting agent to form a homogeneous powder. Different amounts of $CeCO_3$ powder were added to each host phosphate to introduce Ce^{3+} ions into each mixture. All homogeneous powders were annealed at 900 °C for 4 hours. After annealing, each series was further ground to create a fine, uniform powder.

The above-mentioned compounds were combined in accordance with the specified stoichiometric ratios for each series.

$$3\ Na_2CO_3 + 2\ NH_4H_2PO_4 = 2\ Na_3PO_4 + 2\ NH_3 + 3\ CO_2 + 3\ H_2O \tag{1}$$

$$Na_2CO_3 + 2\ BaCO_3 + 2\ NH_4H_2PO_4 = 2\ NaBaPO_4 + 2\ NH_3 + 3\ CO_2 + 3\ H_2O \tag{2}$$

$$Na_2CO_3 + 2\ CaCO_3 + 2\ NH_4H_2PO_4 = 2\ NaCaPO_4 + 2\ NH_3 + 3\ CO_2 + 3\ H_2O \tag{3}$$

$$Na_2CO_3 + 2\ SrCO_3 + 2\ NH_4H_2PO_4 = 2\ NaSrPO_4 + 2\ NH_3 + 3\ CO_2 + 3\ H_2O \tag{4}$$

2.2 *Characterisation*

X-ray powder diffraction was used to characterise the produced nanophosphors (Bruker AXS D8 Advance X-ray diffractometer, Cu Kα, $\lambda = 0.1506$ nm, 40 kV, 40 mA, $10\,° \leq 2\theta \geq 80\,°$). A xenon flash lamp was used as an excitation source in a Cary eclipse fluorescence Varian spectrophotometer to perform the PL spectra measurements. A JEOL JSM-7800F high field emission scanning electron microscope with an EDS was used in this investigation to obtain SEM micrographs of the prepared samples, however the PL emission data was used to determine the colour chromaticity behaviour of the prepared sample.

3 Results and Discussions

3.1 *Powder X-ray diffraction (XRD) analysis*

Figure 1 illustrates the XRD spectra of Na_3PO_4: xCe^{3+} and $NaMPO_4$ nanophosphors (x = 0.0 and 1.0 mol %, M = Ca, Sr, and Ba), indicating a singular crystalline phase in the host and doped Ce^{3+} doped materials. The figure also demonstrates that Na_3PO_4 aligns well with the tetragonal $P\bar{4}21c$ powder diffraction patterns from the PDF#31-1323 [3], but a decrease in intensity is observed when doped with Ce^{3+}. Nevertheless, the intense diffraction peaks appear to shift to lower 2θ angles, indicating an expansion of both crystalline structures resulting from the interstitial substitution of Ce^{3+} ions within the crystal lattice[4]. As the spectra are analysed, the incorporation of Ba^{2+}, Ca^{2+}, and Sr^{2+} alkaline ions into the host lattice enhances crystallinity, as evidenced by the emergence of additional peaks that align well with the JCPDS card patterns for $NaBaPO_4$ (PDF# 33-1210), $NaCaPO_4$ (PDF# 29-1193), and $NaSrPO_4$ (PDF# 33-1282) [5, 6]. However, a significant shift of the prominent peaks towards lower 2θ angles is observed, even for the Ce^{3+} doped samples. The diffraction patterns of the novel host lattices: $NaBaPO_4$, $NaCaPO_4$, and $NaSrPO_4$, correspond well to the monoclinic and orthorhombic phase structures, respectively, in the order presented above.

The inclusion of Ce^{3+} ions to the $NaCaPO_4$ combination results in a reduction in peak intensity. The spectra demonstrate that doping with Ce^{3+} (1.14 Å) ions results in decreased crystallinity without modifying its crystal structure; nevertheless, the reduction in crystallinity may be attributed to the reduced ionic radius of Ca^{2+} ions (1.00 Å).

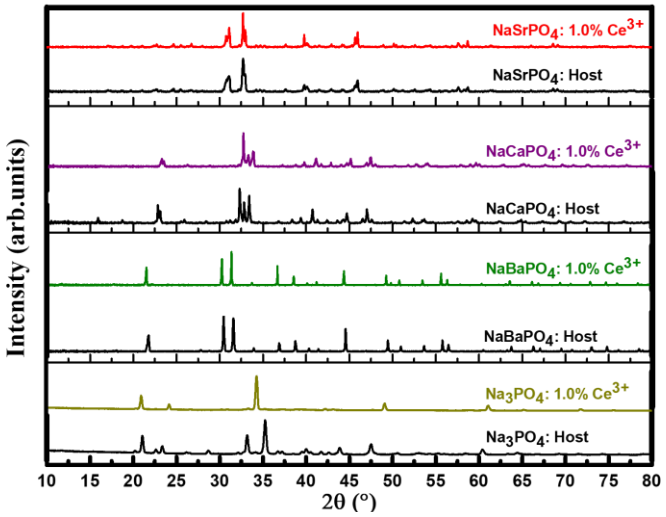

Figure 1: XRD spectra of Na_3PO_4: $x$$Ce^{3+}$ and $NaMPO_4$:$x$$Ce^{3+}$ nanophosphors (x = 0.0, and 1.0 mol %, M= Ca, Sr, and Ba) indicating a single crystalline phase on the host material (Na_3PO_4).

According to the Scherrer equation, the crystalline sizes of the prepared samples were determined and observed to be in the range of 50.5 to 133 nm as presented in Table 1 below. It is observed that $NaBaPO_4$: $x$$Ce^{3+}$ exhibits the most significant particle growth resulting from the Ce^{3+} ions doping. In addition, it also observed the Ba^{2+} alkaline ions presents a significant role to the Na_3PO_4 host lattice itself (check again). One can also observe that Na_3PO_4 and $NaCaPO_4$ exhibit considerable size stability, indicating effective structural accommodation of the Ce^{3+} ions. $NaSrPO_4$ displays a moderate rise, indicating a degree of sensitivity to the incorporation of the dopant.

x mol%	Na_3PO_4:$x$$Ce^{3+}$ size (nm)	$NaBaPO_4$:$x$$Ce^{3+}$ size (nm)	$NaCaPO_4$:$x$$Ce^{3+}$ size (nm)	$NaSrPO_4$:$x$$Ce^{3+}$ size (nm)
0.00	51.2	74.4	50.7	50.7
1.00	50.5	133	50.4	67.0

Table 1: Estimated crystalline sizes of Na_3PO_4:$x$$Ce^{3+}$ and $NaMPO_4$:$x$$Ce^{3+}$ nanophosphors (x = 0.0, and 1.0 mol %, M = Ca, Sr, and Ba).

3.2 Powder Surface morphology and chemical composition analysis

Figures 2 (a), (d), and (g) present the FE-SEM images of $NaBaPO_4$:$x$$Ce^{3+}$, $NaCaPO_4$:$x$$Ce^{3+}$, and $NaSrPO_4$:$x$$Ce^{3+}$ phosphors at x = 0.0 mol%, while Figures 2 (c), (f), and (i) depict the FE-SEM micrographs of $NaBaPO_4$:$x$$Ce^{3+}$, $NaCaPO_4$:$x$$Ce^{3+}$, and $NaSrPO_4$:$x$$Ce^{3+}$ phosphors at x = 1.0 mol%. The SEM images reveal that the particles in the host materials exhibit various sizes and shapes, and the irregularity of the particles becomes more pronounced following doping with Ce^{3+} ions, suggesting an increase in agglomeration due to Ce^{3+} ion incorporation. The SEM host micrographs indicate that $NaBaPO_4$ particles are larger and more irregular than those of $NaCaPO_4$ and $NaSrPO_4$ materials and this is also evidenced in Table 1 above. The morphology of these materials tends to cluster and resembles a dried paste following Ce^{3+} ion doping, as illustrated in Fig. 2 (c), (f), and (g). This is due to the distortion of particle morphology caused by Ce^{3+} ion impurities under identical temperature conditions maintained for the host materials [7].

The analyzed materials were subjected to EDS spectroscopy to ascertain the presence of various elements in the synthesized phosphors. The EDS spectra of $NaBaPO_4$:$x$$Ce^{3+}$, $NaCaPO_4$:$x$$Ce^{3+}$, and $NaSrPO_4$:$x$$Ce^{3+}$ phosphors, with x = 0.0 and 1.0 mol%, are presented in Fig. 2, (b), (e), and (h), respectively. The EDS spectra of these phosphors validated the existence of distinct elements, including Na, O, P, Ba, Ca, Sr, and Ce atoms. This is further confirmed by the clearly defined intensity peaks of the individual elements.

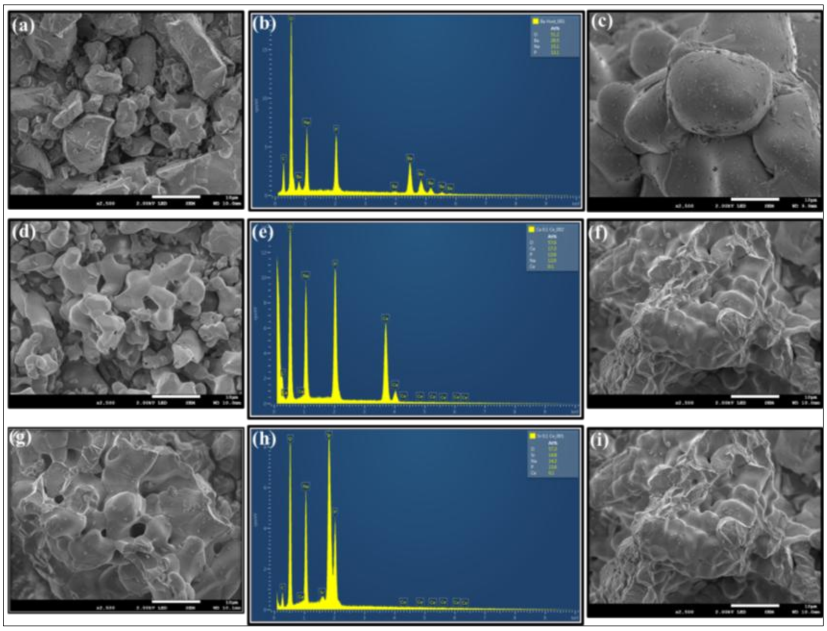

Figure 2: SEM micrographs of: (a) $NaBaPO_4$, (c) $NaBaPO_4$:1.0%Ce^{3+}, (d) $NaCaPO_4$, (f) $NaCaPO_4$:1.0%Ce^{3+}, (g) $NaSrPO_4$, and (i) $NaSrPO_4$:1.0%Ce^{3+} demonstrating high agglomerated, fine, and irregular shaped particles. Figure 5 (b), (e), and (h): EDS spectra confirming the relevant elements: Ba, Ca, and Sr respectively with Na, O, and P.

3.3 Photoluminescence studies

The excitation spectra (PLE) of $Na_3PO_4{:}xCe^{3+}$ and $NaMPO_4{:}xCe^{3+}$ phosphors (where x = 0.0 and 1.0 mol %, M = Ba, Ca, and Sr) were recorded throughout the range of 225-360 nm, while observing the prominent emission peak at 385 nm, as illustrated in Figure 3 (a). This spectrum reveals three wide PLE intensity peaks within the wavelength region of 230-300 nm. The three excitation bands mostly result from the 4f → 5d transition between the energy levels of the Ce^{3+} ion [8]. The insert in Figure 3 (a) indicates that $Na_3PO_4{:}xCe^{3+}$ does not react to the excitation wavelength of Ce^{3+}, likely due to the absence of alkaline metal ions that may promote energy transfer to or from the dopant. The excitation intensity bands of the Ce^{3+} ion is markedly enhanced in the 1.0 mol% Ce^{3+}-doped $NaBaPO_4$ material, likely due to the ionic radii relationship between Ce^{3+} and Ba^{2+} ions [9].

The intense band at 281 nm was deemed suitable for recording the emission spectra of the $NaMPO_4{:}xCe^{3+}$ samples, where x = 0.0 and 1.0 mol %. The photoluminescence spectra of $Na_3PO_4{:}xCe^{3+}$ and $NaMPO_4{:}xCe^{3+}$ were recorded in the 300-500 nm range using a 281 nm UV excitation wavelength, as illustrated in Figure 3(b). Only one emission band was seen at a wavelength of 385 nm, which can be attributed to the 5d→4f transition between the energy levels of the Ce^{3+} ion. The emission bands of 1.0 mol% Ce^{3+} ions in $NaBaPO_4$ are markedly higher than those of the other samples, with 1 mol% for $NaBaPO_4$ followed by 1 mol% Ce^{3+} doped in $NaCaPO_4$, attributable to the differing ionic radii. The insert in Figure 3b indicates no emission from the $Na_3PO_4{:}xCe^{3+}$ material, and this is likely attributed to the lack of alkaline metal ions [10].

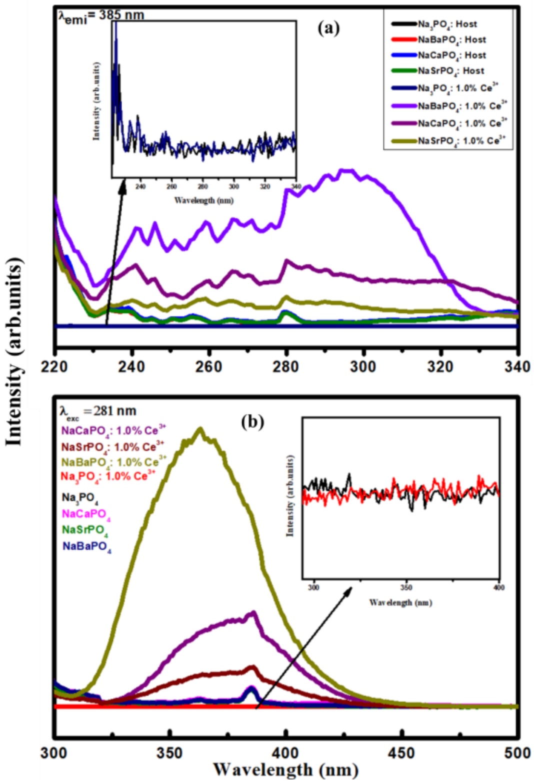

Figure 3: (a) PL excitation spectra of Na_3PO_4: $x$$Ce^{3+}$ and $NaMPO_4$: $x$$Ce^{3+}$ nanophosphors (x = 0.0, and 1.0 mol %, monitored at λ_{emi} = 385 nm. (b) PL emission spectra of Na_3PO_4: $x$$Ce^{3+}$ and $NaMPO_4$: $x$$Ce^{3+}$ nanophosphors (x = 0.0, 1.0 mol % and M = Ca, Sr, and Ba) monitored at λ_{exc} = 281 nm.

3.4 Commission International de l'Eclairage (CIE)- colour coordinates

Figure 4 presents the CIE plots of $NaMPO_4$:$x$$Ce^{3+}$ phosphors, with x values of 0.0 and 1.0 mol %, and M representing Ca, Sr, and Ba. According to the CIE chromaticity diagram, all color coordinates for orthophosphate materials are situated within the blue-to-violet spectrum of the color range. The color coordinates of $NaMPO_4$ host materials emit light in the pure blue area; however, a shift towards the violet region occurs upon doping with Ce^{3+} ions [11]. The Na_3PO_4:$x$$Ce^{3+}$ material is absent from the figure, which aligns well with the PL emission spectra shown in Figure 3 (b). The results suggest that the synthesized phosphor materials are viable options for bluish-violet color-emitting applications in colour display systems.

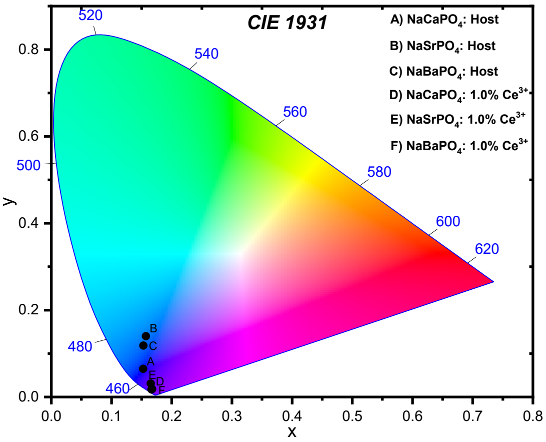

Figure 4: CIE chromatic-diagram of $NaMPO_4$: $x$$Ce^{3+}$ nanophosphors (x = 0.0, and 1.0 mol %, M= Ca, Sr, and Ba)

4 Conclusion

This study explored the Na_3PO_4:$x$$Ce^{3+}$ and $NaMPO_4$:$x$$Ce^{3+}$ samples with concentrations x = 0.0 and 1.0 mol %, where M represents alkaline Ba, Ca, and Sr, synthesized via the solid-state reaction technique. This study examined the structural and optical properties of the synthesized samples. XRD examinations revealed that the synthesized materials crystallized into a tetragonal structure, which subsequently transformed into monoclinic and orthorhombic phase structures, as detailed in the preceding XRD analysis section. SEM investigations confirmed that particle agglomeration was observed with Ce^{3+} ion doping. The photoluminescence spectra were obtained using a 281 nm excitation wavelength, revealing a singular emission band at 385 nm. The PL data and CIE color diagram results confirm that the current materials may serve as viable choices for violet color-emitting devices.

References

[1] M.B. Bechir, M.H Dhaou, Synthesis, optical and dielectric properties of orthophosphate M_3PO_4 (M = Li, Na) compounds, *SSRN*, 2018.

[2] K.N. Shinde, S.J. Dhoble, H.C Swart and K. Park, Phosphate phosphors for solid-state lighting, *Springer series in materials science*, volume 174, 2012.

[3] J. Zhou, S Lin, L. Deng, Jun Li, T Zeng, Z. Huang, H. Huang, Performance study of Na_3PO_4-expanded graphite composites for lowtemperature thermochemical heat storage, *Energy Proceedings*, Vol. 55, 2025.

[4] J.G.O. Netoa , O.C.S. Netoa , F. Pedrochi, A. Steimacher, J.S. Filhoa , F.F. de Sousa, L.M. Silva, A.O. Santos, Structural, vibrational, thermal, and optical properties of L-threonine crystals containing Ce^{3+} ions, *Journal of Molecular Structure*.Vol 1254, 2022.

[5] Chen, K.H., Weng, M.H., Pan, C.T., Yang, R.Y., Effect of different sintering method on the microstructure and photoluminescent properties of $NaSrPO_4$:Tb^{3+} phosphors, Powder Technology, 288, 2016, 117-122.

[6] Chen, K. H., Weng, M. H., Pan, C. T., and Yang R. Y., Crystal structure and luminescent properties of Tb^{3+}, Ce^{3+}, and codoped NaSrPO4 phosphors prepared by microwave sintering, *Sensors and Materials*, Vol. 29, 1607–1614, 2017.

[7] A.P. Sefage, The Effect of Ce^{3+} on the Luminescence Properties of the $ABPO_4$ (A= Na, B = Mg, Ca, Sr, and Ba) Using the Solid-State Reaction Method, Johannesburg: University of Johannesburg, Available from https://hdl.handle.net/10210/499121. 2021.

[8] I. A.M Ibrahim, Z. Lenčéš, P. Šajgalík, L. Benco, and M.Marsman, Electronic structure and energy level schemes of RE3+ :$LaSi_3N_5$ and RE^{2+} :$LaSi_3N_{5-x}O_x$ phosphors (RE= Ce, Pr, Nd, Pm, Sm, Eu) from first principles, *Journal of Luminescence*, 164, 2015, 131-137.

[9] C.Gu, and D.M.F. Cooper, Ca^{2+}, Sr^{2+}, and Ba^{2+} identify distinct regulatory sites on adenylyl cyclase (AC) types VI and VIII and consolidate the apposition of capacitative cation entry channels and Ca^{2+}-sensitive ACs, *Journal of Biological Chemistry*, Vol. 275, no. 10, pp. 6980–6986, 2000

[10] A. Balakrishna, L. Reddy, O.M. Ntwaeaborwa , H.C. Swart, Remarkable influence of alkaline earth ions on the enhancement of fluorescence from Eu^{3+} ion doped in sodium ortho-phosphate phosphors, *Journal of Molecular Structure,* Vol. 1203. 2020.

[11] B. Yuan, J. Gou, C. Qi, L. Kong, M. Qu, G. Luana, and X. Zhang Energy transfer for Ce^{3+} / Tb^{3+} / Sm^{3+} induced bright white emission in single-phase $CaLa_4(SiO_4)_3O$:Ce^{3+}, Tb^{3+}, Sm^{3+} phosphors and their application in white-light-emitting diodes, *Royal Society of Chemistry*. Vol. 14. 2024.