

The Effects of Synthesis Techniques on the Photoluminescent Behaviours of the $\text{NaMPO}_4:\text{Ce}^{3+}$ (M=Mg, Ca, Ba, Sr) Nanophosphors

Leelakrishna Reddy¹, Balakrishna Avula¹, Amanda Percy Sefage¹, Prettier Morongoa Maleka² and Martin Ntwaeaborwa²

¹University of Johannesburg

²University of the Witwatersrand

Johannesburg, South Africa

krishr@uj.ac.za

Abstract - Researchers are in active pursuit of scintillator materials for diagnostic applications in medical science. Such pursuits are only achieved through experimental investigations of phosphor materials. To address this issue, we focused on the comparative photoluminescent behaviours of inorganic orthophosphates, $\text{NaMPO}_4:\text{xCe}^{3+}$ (M = Ca, Ba, Sr, Mg), synthesized via the traditional solid-state reaction method and the combustion method. The combustion method is a simple and rapid method of producing a variety of nanosized particles (use of nitrates, fuels, etc.), while the solid-state reaction method (use of metal oxides) focus on a gradual heating of the powders from room temperature to 900 °C (to allow for interdiffusion of cations). Various techniques such as XRD, SEM and PL were used to characterize these phosphor materials. Further, the CIE (Commission international de l'éclairage) plots were then obtained using the PL data to compare colour tuning in each case. A comparison of the results reveals that the $\text{NaBaPO}_4:\text{xCe}^{3+}$ phosphor displayed the best photoluminescence behaviour for an optimal concentration of $x = 0.5$ mol % using the combustion method of synthesis, on the other hand using the solid-state reaction method, the best photoluminescence was obtained for an optimal concentration of $x = 1$ mol % for the same material. In each of the above cases, the PL emission spectra was due to the $5d \rightarrow 4f$ transition of the Ce^{3+} ions. The results points to the fact the Ce^{3+} emissions in the $\text{NaBaPO}_4:\text{xCe}^{3+}$ ion occurs for a higher concentration in the solid-state method and for a lower concentration in the combustion method scenario (quenched for same concentration in the combustion method). This could be attributed to the slow diffusion of ions in the solid-state reaction method, compared to the fast combustion in the combustion method (600 °C).

Keywords: phosphor, luminescence, scintillator, and rare-earth ions

1. Introduction

Recently there has been rapid growth in research of phosphor materials for its wide range of luminescence applications in solid-state lighting devices [1,2]. Of particular interest, orthophosphates with formula of ABPO_4 (with A= alkaline metals and B = alkaline earth metals) has attracted much interest because of its intense luminescence emissions in the visible region and facile methods of preparation making them potential candidates for applications in colour display devices [3,4]. In the preparation of such materials, it is envisaged that by varying the alkaline earth metals (B = Ba, Ca, Mg and Sr) in the host lattice, and by doping it with Ce^{3+} ion, the emission efficiency could be drastically improved [5]. Ce^{3+} ion is a preferred dopant because it allows for fast fluorescent $5d \rightarrow 4f$ emission in the UV region of the electromagnetic spectrum [6]. There are many methods (temperature variations) to prepare these phosphor materials and they range from the sol-gel, hydrothermal, co-precipitation, combustion and to the solid-state reaction method. In this study, we have considered the $\text{ABPO}_4:\text{Ce}^{3+}$ phosphor materials synthesized via the combustion and solid-state reaction methods. Further, we have focused on the impact on the synthesis method on the photoluminescence behaviour of the same material using different techniques.

2. Experimental Techniques

Orthophosphates of the nature $ABPO_4:Ce^{3+}$ has been considered for this study, using the combustion and solid-state reaction techniques as a method of comparison.

2.1. The Combustion Technique

All materials used for this technique were purchased from Sigma-Aldrich and were of AR grade (99.99 %) purity. Materials were prepared according to the stoichiometric formula: $ABPO_4:xCe^{3+}$ (with A = Na, B = Ba, Ca, Mg, Sr, and x = 0.5, 1.0 and 1.5 mol %). The cerium ion used in this study came from the $CeNO_3$ powder. Raw powder materials were ground in an agate mortar and further dissolved in de-ionized water to obtain a homogeneous material. Molar ratios of the rare-earth ions were varied in accordance with the respective Mg/Ca/Ba/Sr ions in the phosphor material. The various compositions of the metal nitrates (oxidizers) together with the fuel (urea) used for the combustion process were calculated by combining the total oxidizing and reducing valences of the various components so that the heat liberated for the process is maximized. Each mixture was vigorously stirred for 90 minutes over a magnetic stirrer, set at 100 °C to obtain a homogeneous solution, and thereafter placed into a muffle furnace, pre-heated at 600 °C for the combustion process to take place. The sample was combusted for a short time of 5 minutes until a foam-like product was produced. This powder like product was then ground again for uniformity of grain size which was then made ready for characterization process to take place.

2.2. The Solid-State Reaction Technique

All samples required for the preparation using this technique for the $ABPO_4:xCe^{3+}$ phosphors (x = 0.1, 0.5, 1.0, 1.5. and 2 mol %) were of AR grade (99.99 %) purity, which was purchased from Sigma Aldrich in Germany. The compounds, using the solid-state reaction route, need to be in the oxide or carbonate state. Stoichiometric amounts of the starting materials were combined and ground into powders with additions of acetone to ensure homogeneity in the product. The final product was then placed in an alumina crucible and then placed into a muffle furnace, heated from room temperature to 900 °C for all samples except the $NaMgPO_4:Ce^{3+}$ sample which was heated to 780 °C for a total period of 4 hours. The final product was then allowed to cool down to room temperature and with subsequent grinding, the sample was then made ready for the characterization process.

2.3. Characterizations

All samples were sent for various characterizations such as X-Ray Diffraction (XRD), Scanning Electron Microscopy (SEM), Fourier Transform Infrared spectroscopy (FTIR), Photoluminescence (PL), Fluorescence decay and UV-visible measurements. This study will only focus on the XRD, SEM, PL, and CIE measurements on the comparative techniques. Here CIE (Commission International de l'Eclairage) uses the PL data to plot CIE colour coordinate diagram.

3. Results and Discussion

From our previous research work [5,7,8], it has been confirmed that of all $ABPO_4:xCe^{3+}$ (A = Na, B = Ca, Ba, Mg and Sr) phosphor materials, $NaBaPO_4:xCe^{3+}$ phosphor produced the highest luminescence properties for x = 1 mol % for the solid-state reaction method and in the case of the combustion method, highest luminescence was achieved for x = 0.5 mol %. Analysis of results will henceforth focus on these two phosphors as main compounds, but in the case of the PL properties other concentrations are included.

3.1. XRD and SEM results of the $NaBaPO_4:xCe^{3+}$ phosphor material

Figures 1(a) and 1(b) shows the XRD spectra of the $NaBaPO_4:xCe^{3+}$ phosphor material for x = 1 mol % [7] and x = 0.5 mol % [8] prepared by the solid-state reaction and combustion methods, respectively.

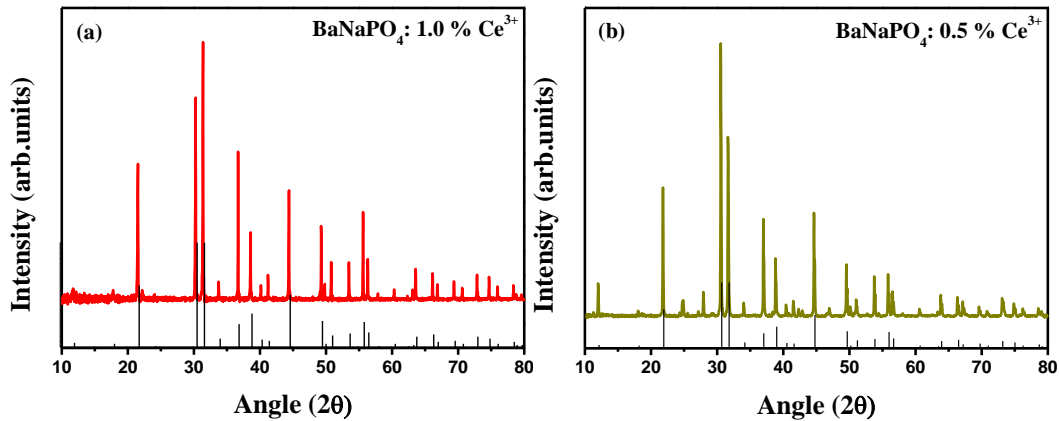


Fig. 1: X-ray diffraction spectra of the $\text{NaBaPO}_4:\text{xCe}^{3+}$ phosphors prepared by the (a) solid-state reaction ($x = 1 \text{ mol } \%$) and (b) combustion ($x = 0.5 \text{ mol } \%$) methods.

A comparison of the XRD results show that the solid-state reaction method is more matchable with the background data compared to the combustion method. In the case of the combustion diffraction data, few impurities are observed. In both cases, the $\text{NaBaPO}_4:\text{Ce}^{3+}$ phosphors crystallized into an orthorhombic structure with a space group of $P-3m1m$ [5,7,8]. It has been observed that the incorporation of the Ce^{3+} ion did not affect the diffraction patterns of both synthesis methods, implying that a homogeneous mixture is produced. The reason for this is that Ba^{2+} ion of ionic radius 1.42 \AA is displaced by Ce^{3+} ion of radius 1.14 \AA during the doping and synthesis process. To further remove the impurities in the $\text{NaBaPO}_4:\text{xCe}^{3+}$ phosphor for the $x = 0.5 \text{ mol } \%$, it is necessary to anneal it for longer periods to obtain the matchable diffraction patterns as obtained in the case of the solid-state reaction method.

Figure below 2(left image) [7] and 2(right image) [8] show the SEM spectra of the $\text{NaBaPO}_4:\text{xCe}^{3+}$ phosphors for $x = 1 \text{ mol } \%$ and $x = 0.5 \text{ mol } \%$, prepared by the solid-state and combustion methods, respectively. A comparison of the SEM results indicates the solid-state reaction method produces a compact agglomerated particle morphology with particle sizes in the micrometer dimensional range. In the case of the combustion process of synthesis, particles of irregular size and shapes (rods, plates, etc.) are produced. Grain sizes are also in the micrometer dimensional range. Evidence of gaps as seen in this case, are due to escaping gases during the combustion process.

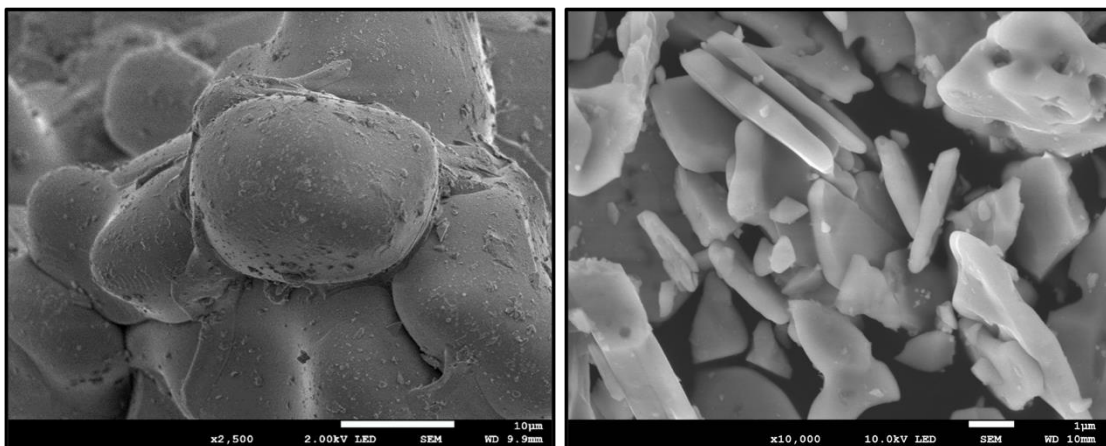


Fig. 2: SEM spectra of the $\text{NaBaPO}_4:\text{xCe}^{3+}$ phosphor material, prepared by the solid-state reaction (left image above for $x = 1 \text{ mol } \%$) and combustion (right image above for $x = 0.5 \text{ mol } \%$) methods, respectively.

3.2. Photoluminescence (PL) properties of the NaBaPO₄:xCe³⁺ phosphor materials using the solid-state reaction method

3.2.1. Photoluminescence Excitation Spectra

The excitation spectra of the NaBaPO₄:1.0 Ce³⁺ phosphor is shown in figure 3(a), monitored under an excitation wavelength of 385 nm (see emission spectra). The excitation spectra consist of roughly two broad bands in the spectral region from 230 nm to 310 nm [7].

When Ce³⁺ ion is doped into the host NaBaPO₄ material, the rare-earth ion lies in the bandgap of its host. Ce³⁺ ion has an electronic ground state of Ce [Xe]4f¹5d⁰ and accounts for the absorption and emission observed. Due to spin-orbit coupling, the 4f energy level is split into doublet states, namely ²F_{5/2} (lower energy level) and ²F_{7/2} (upper energy level). When cerium is excited from its ground state, the one cerium electron moves from the 4f energy level to the 5d¹ energy level (Ce [Xe]4f⁰5d¹) and is influenced by the crystal field of the host material. Cerium ion, combined with the phosphate material is found to emit light in the UV region of the electromagnetic spectrum.

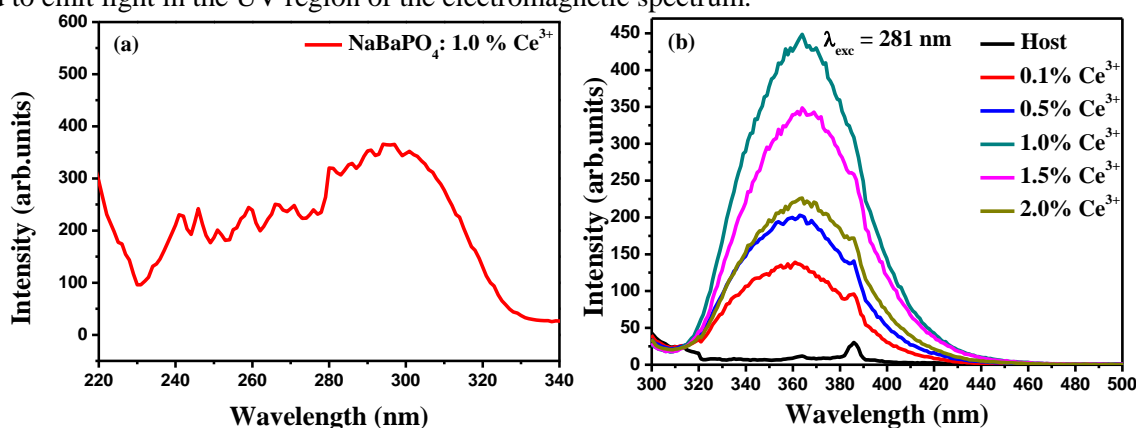


Fig. 3: (a) PL excitation spectra of NaBaPO₄:1.0% Ce³⁺ phosphor material, monitored at 385 nm wavelength of light and (b) the PL emission spectra of NaBaPO₄:xCe³⁺ (x = 0.1, 0.5, 1.0, 1.5 and 2.0 mol %) phosphor material, excited at 281 nm wavelength of light (solid-state reaction method).

3.2.2 Photoluminescence Emission Spectra

The emission spectra of the NaBaPO₄:xCe³⁺ phosphor materials for x = 0.1, 0.5, 1.0, 1.5. and 2 mol % is shown in figure 3 (b), monitored under an excitation wavelength of 281 nm (see excitation spectra) [7]. The emission spectra, which lies in the UV spectral region from 300 to 400 nm is due to the transition from the 5d state to the 4f state of Ce³⁺ ion. The emission bands in Ce³⁺ ion generally has a doublet nature due to the downward transition of cerium electron from higher excited states to lower states (²F_{5/2} and ²F_{7/2}). However, in the case of the solid-state reaction method, we see some of the doublet states, namely a transition to the ²F_{7/2} at around 385 nm and further downward transition to the ²F_{5/2} state at around 360 nm for x = 0.1 and 0.5 mol % Ce³⁺ ion concentrations, respectively. For higher concentrations, we see the dominance of the transition to the ²F_{5/2} state but the downward transition to the ²F_{7/2} state becomes weak and then disappears. The emission intensity increases from x = 0 mol % up to a maximum intensity of x = 1 mol % Ce³⁺, thereafter the intensity is quenched. The disappears of this type of transition maybe attributed reabsorption of emission [9] by atoms surrounding the Ce³⁺ ions or by trapping mechanisms such as self-trapped excitons, hole traps or electron traps [6].

3.3 Photoluminescence (PL) properties of the NaBaPO₄:xCe³⁺ phosphor materials using the combustion method

3.3.1. Photoluminescence Excitation Spectra

The excitation spectra of the NaBaPO₄:0.5Ce³⁺ phosphor is shown in figure 4(a), monitored under an excitation wavelength of 378 nm (see emission spectra). The excitation spectra consist of two prominent peaks, one at 251 nm and the other at 300 nm [5, 8]. These peaks are due to 4f → 5d transitions in Ce³⁺ ion.

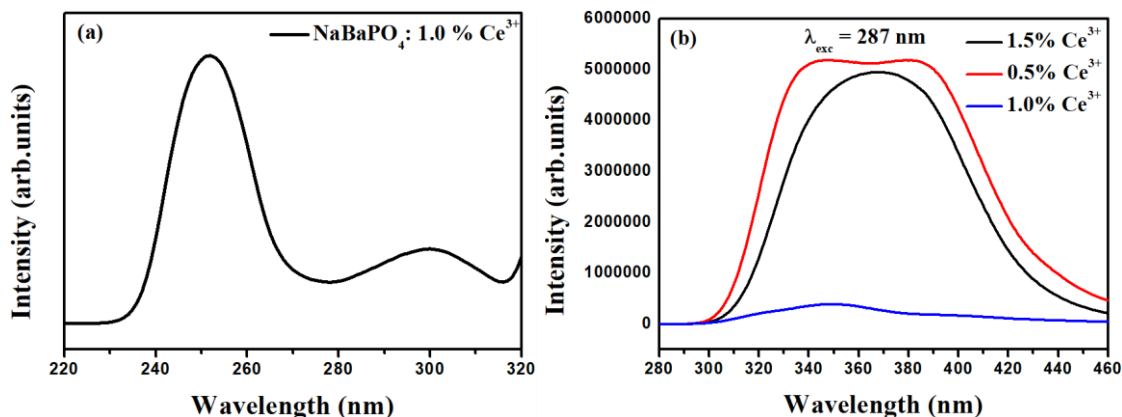


Fig. 4: (a) PL excitation spectra of $\text{NaBaPO}_4: 0.5\text{Ce}^{3+}$ phosphor material, monitored at 378 nm wavelength of light and (b) the PL emission spectra of $\text{NaBaPO}_4:x\text{Ce}^{3+}$ ($x = 0.5, 1.0$ and 1.5 mol %) phosphor material, excited at 287 nm wavelength of light (combustion method).

3.3.2. Photoluminescence Emission Spectra

The emission spectra of the $\text{NaBaPO}_4:x\text{Ce}^{3+}$ phosphor material for $x = 0.5, 1.0$ and 1.5 mol % is shown in figure 4(b), monitored at a wavelength of 287 nm of light [5, 8]. The emission spectra show an increase in emissions ranging from $x = 1.0$ mol % (lowest) to 1.5 mol % (middle) and to the highest emission for $x = 0.5$ mol % of Ce^{3+} ion. The doublet nature of emission is evident for the $x = 0.5$ mol % concentration of Ce^{3+} ion. The shape of the curve for $x = 0.5$ mol % can lead to two deconvoluted peaks by Gaussian fitting (asymmetric), and this will mean that the Ba^{2+} ion site could be replaced by Ce^{3+} ion of similar ionic radius, leading to increased number of luminescent centers, thereby enhancing the luminescent characteristics of the phosphor material. Thus, the downward transitions to the doublet states (${}^2\text{F}_{5/2}$ at 336nm and ${}^2\text{F}_{7/2}$ at 380 nm) are very possible for this phosphor material. However, this downward transition trend appears to vanish for other concentrations, leading to symmetric emissions curves.

A comparison of the synthesis methods reveals that the highest luminescence for the solid-state reaction occurs at $x = 1$ mol %, while in the case of the combustion method the highest luminescence occurs for $x = 0.5$ mol % of Ce^{3+} ion concentration. At face value it would appear that better luminescence occurs for the solid-state reaction method, since at $x = 1$ mol % of Ce^{3+} ion concentration that emission intensity is quenched for the combustion method. In the next figure we have combined the concentration of both methods for $x = 0.5$ and 1 mol % Ce^{3+} ion concentrations to make a better judgement.

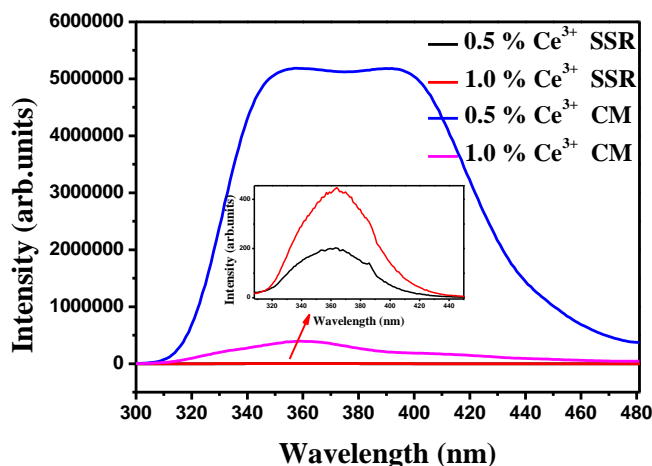


Fig. 5: PL emission spectra of the $\text{NaBaPO}_4:\text{xCe}^{3+}$ phosphor material for $x = 0.5$ and 1 mol %, prepared by the solid-state (SSR) and combustion methods (CM).

Figure 5 [5,7,8] shows the combined emission spectra of the $\text{NaBaPO}_4:\text{xCe}^{3+}$ phosphor material, prepared by two synthesis methods. It is clear from figure 5 that the combustion method of synthesis produces a remarkably high luminescence emission intensity for $x = 0.5$ mol % Ce^{3+} ion concentration (even $x = 1.5$ mol % of Ce^{3+} ion concentration would be just as good). Although the solid-state reaction method of synthesis involves prolonged temperature (5 hours as opposed 5 minutes) measurements, it might be that excess oxygen vacancies are created in the host through this process, leading to quenching of luminescence [6, 10]. Although oxygen vacancies are good because it acts as a sensitizer in allowing for the transfer of energy to Ce^{3+} ion through the mixture of charge transfer states, the effect of which is enhanced luminescence characteristics of the phosphor material [6,10], but excess of it could be detrimental to the crystallinity of the material. It would appear that the Ba^{2+} ion replacement by Ce^{3+} ion as luminescent centers compared to oxygen vacancies has a more dramatic effect on the luminescence properties of this material.

3.4 Commission Internationale de l'éclairage (CIE)

CIE, which is commonly known as colour chromaticity, uses the PL data to obtain the colour coordinates of the phosphor material (use of CIE 1931 model) [7, 8]. Figure 6 shows the CIE chromaticity coordinates for colour emissions in the $\text{NaBaPO}_4:\text{xCe}^{3+}$ phosphor material for $x = 1$ mol % (solid-state reaction method) and $x = 0.5$ mol % (combustion method) concentrations.

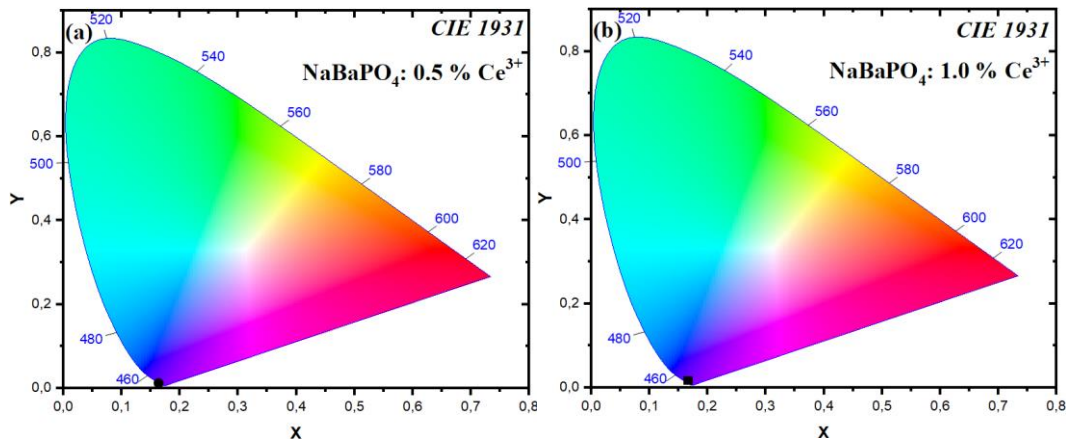


Fig. 6: CIE chromaticity coordinates diagram of the $\text{NaBaPO}_4:\text{xCe}^{3+}$ phosphor material for (a) $x = 0.5$ mol % (combustion method) and (b) $x = 1.0$ mol % (solid-state reaction method) concentration.

From figure 6, it is observed that that the colour emission in both cases lie in the deep blue to violet region of the electromagnetic spectrum. In the case of $x = 0.5$ mol % of Ce^{3+} , the colour shift is deeper into UV region. Phosphor materials containing rare-earth ions and when doped in the host material produces UV emissions due to $5d \rightarrow 4f$ transitions become suitable materials for scintillation applications [9]. Thus, in this case the $\text{NaBaPO}_4:0.5\% \text{Ce}^{3+}$ phosphor materials would be an ideal phosphor for scintillation applications as produced through the combustion method of synthesis.

4. Conclusion

The $\text{NaBaPO}_4:\text{xCe}^{3+}$ phosphor material has been prepared by the solid-state reaction and combustion methods of synthesis. XRD measurements confirmed an orthorhombic crystal structure formation for the prepared phosphor materials. The luminescence characteristics of these materials was found to vary with concentration and type of synthesis methods used in its preparation. The $\text{NaBaPO}_4:0.5\% \text{Ce}^{3+}$ phosphor material has produced remarkable emissions when synthesized via the combustion method as compared to the $\text{NaBaPO}_4:1.0\% \text{Ce}^{3+}$ phosphor material when prepared by the solid-state reaction method. Evidence of doublets peaks, centered at 360 nm and 385 nm, corresponding to $5d \rightarrow {}^2F_{5/2}$ ($4f$) and

$5d \rightarrow {}^2F_{7/2}$ ($4f$) transitions, respectively was observed for the $\text{NaBaPO}_4:0.5\% \text{Ce}^{3+}$ phosphor material, making it an ideal material for scintillation application. The competitiveness between the processes that account for enhanced emissions to the mechanisms that accounts for quenching needs to be further explored in developing materials that could be used as scintillation devices for diagnostic medical applications.

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