



SYNTHESIS AND CHARACTERISATION OF METAPHOSPHATE

$\text{NaCe}(\text{PO}_3)_4:\text{Dy}^{3+}$

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ABSTRACT

Inorganic Phosphor $\text{NaCe}(\text{PO}_3)_4:\text{Dy}^{3+}$ was synthesized by solid state diffusion method. The prepared sample was characterized by X-Ray diffraction and Photoluminescence. The Photoluminescence study shows doped Dy^{3+} leads to a significant increase in the emission intensity in the range of 500-600nm. This is due to the efficient energy transfer from Ce^{3+} to Dy^{3+} under an excitation of 254 nm. Such phosphors can be used for UV lamps application, in solid state Lasers and in optical amplifiers.

INTRODUCTION

Rare Earth doped inorganic phosphors are used extensively in solid state lighting, because they have long life, physical and chemical stability and environment friendly nature. The lanthanide ions like Tb^{3+} and Dy^{3+} in ortho and meta-phosphates give a high quantum yield of visible Luminescence. Trivalent lanthanide ions are used extensively for optically-pumped solid-state lasers because they possess suitable absorption bands and numerous fluorescence lines of high quantum efficiency in the visible and near-infrared. Sensitization of characteristic fluorescence is a well known phenomenon on which a large number of experimental studies have been published. Ce^{3+} has a strong absorption in many hosts and emission matching with $4f^n$ levels of other rare earth impurities, and thus it can be used as a sensitizer for Tm^{3+} , Sm^{3+} , Dy^{3+} , Tb^{3+} , Nd^{3+} , Gd^{3+} , and Pr^{3+} . In this paper Photo-luminescence in $\text{NaCe}(\text{PO}_3)_4$ and $\text{NaCe}(\text{PO}_3)_4:\text{Dy}^{3+}$ has been reported. Energy transfer phenomena have lead to the development of new and efficient photoluminescence materials.



Inorganic phosphors containing Dy^{3+} ions show luminescence lines in the 470–500 nm region due to the ${}^4F_{9/2} - {}^6H_{15/2}$ transition and in the 570–600 nm region due to the ${}^4F_{9/2} - {}^6H_{13/2}$ transition. These have attracted much attention because of their white light emission [1–3]. Dy^{3+} ions in the visible (400–600 nm) region of the spectra have attracted much attention because of their white light emission [4–7]. The Ce^{3+} ion can be used as sensitizer as well as an activator, depending on the splitting of 5d excited levels by the crystal field symmetry. Much work has been done on the energy transfer from Ce^{3+} to different activator ions in different host lattice. Dy^{3+} emission falls mainly in two lines in the visible region arising from ${}^4F_{9/2} \rightarrow {}^6H_{15/2}$ (470–500 nm) and ${}^4F_{9/2} \rightarrow {}^6H_{13/2}$ (570 nm) transitions. The relative intensities of the two bands depend on the local symmetry. When the ratio of blue to green emission is appropriate, one can obtain white emission using Dy^{3+} . This property has generated some interest in Dy^{3+} luminescence. UV cannot efficiently excite Dy^{3+} because its CT state as well as the 5d levels are situated above 50,000 cm^{-1} . Dy^{3+} can be sensitized by Bi^{3+} , Gd^{3+} , Ce^{3+} , Pb^{2+} and vanadate ions.

EXPERIMENTAL

$NaCe(PO_3)_4$ has been obtained from the binary system $CePO_4$ and Na_3PO_4 . $NaCe(PO_3)_4$ has been synthesised by sintering the mixture of $Ce(PO_3)_3$ and $NaPO_3$ in the molar ratio 1:1 at 750°C for 20 hr. Cerium meta phosphate $Ce(PO_3)_3$ was obtained from cerium oxide CeO_2 and $NH_4H_2PO_4$ by sintering the mixture of these compounds stoichiometrically at 250, 500 and 900°C for 2, 5, and 15 hr respectively. Sodium meta phosphate $NaPO_3$ was obtained by complete dehydration of $NaH_2PO_4 \cdot H_2O$ at 300°C for 0.5 hr and then at 500°C for 2 hr. Method given by Szczygiel et al and Rzaigui [8,9] were followed for preparation of this compound. While preparing $NaCe(PO_3)_4:Dy$ the constituents $Ce(PO_3)_3$ and $NaPO_3$ and sulphate salt of dysprosium were taken in a

stoichiometric ratio and crushed in a crucible for 1 hr. Then this material was heated at 750°C for 20 hr, resulting in the compound $\text{NaCe}(\text{PO}_3)_4:\text{Dy}$ in powder form. The samples were then slowly cooled at room temperature. The resultant polycrystalline mass of each sample was crushed to fine particle in a crucible. This powder form was used in further study. X-ray diffraction patterns were recorded on Philips PANalytical X'pert Pro diffractometer. Photoluminescence (PL) spectra in the spectral range 220-700 nm were recorded at room temperature on Hitachi F-4000 spectro-fluorimeter with spectral slit widths of 1.5 nm.

RESULTS AND DISCUSSIONS

Fig.1 shows the XRD of prepared $\text{NaCe}(\text{PO}_3)_4$. X-ray diffraction of prepared $\text{NaCe}(\text{PO}_3)_4$ is found to match with ICDD file 33-1233 of $\text{NaCe}(\text{PO}_3)_4$.

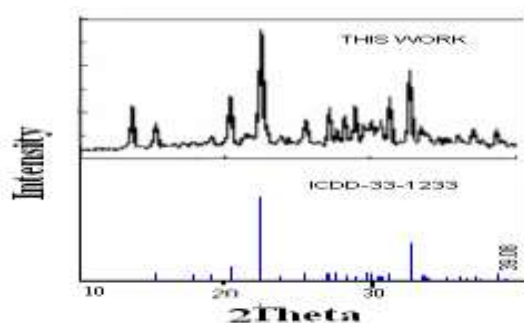


FIGURE1. XRD of $\text{NaCe}(\text{PO}_3)_4$.

PL emission and excitation result of $\text{NaCe}(\text{PO}_3)_4$:

The emission spectra of the prepared $\text{NaCe}(\text{PO}_3)_4$ is also recorded using a spectral slit of 5, 1.5 nm and excitation spectra is recorded using a spectral slit of 1.5, 1.5 nm. {Fig.2 curves (a)&(b)}. The **emission** spectra {curve(b)} shows intense PL emission with peaks at 346 nm (28901cm^{-1} , 3.59 eV) and 327.6 nm (30525cm^{-1} , 3.79 eV) which are due to transition from the lowest level of 5d configuration to the two $^2\text{F}_{5/2}$, $^2\text{F}_{7/2}$ multiples of the $4f^1$ configuration in **Ce³⁺** ions and half intensity peaks at 316

nm(31645 cm^{-1} , 3.94 eV) and 361 nm (27701 cm^{-1} , 3.44 eV). The PL **excitation** { curve(a)} shows a broad band in the range 220 nm to 320 nm with peak at 298.6 nm (33489 cm^{-1} , 4.16 eV), 254.4 nm (39308 cm^{-1} , 4.88 eV) and 227.6 nm (43936 cm^{-1} , 5.46 eV) and Half intensity peaks at 310 nm (32258 cm^{-1} , 4 eV) and 282 nm (35461 cm^{-1} , 4.40 eV). From these results, the Stokes shift amounts to about (2964 cm^{-1}) .

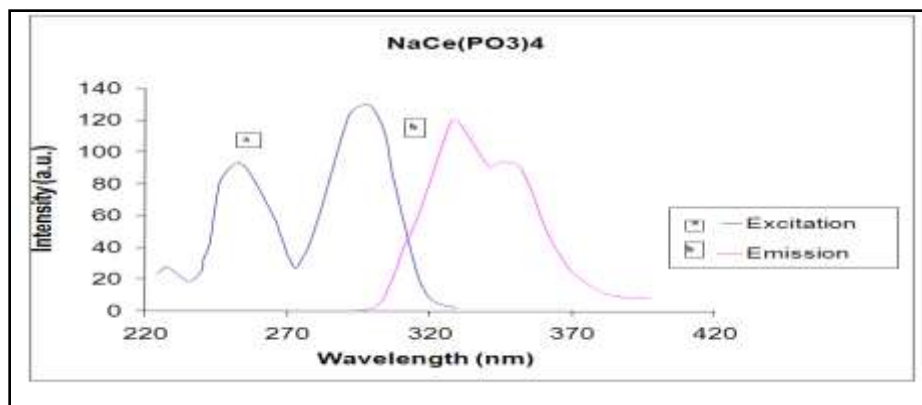


Figure2: a Excitation for 346 nm emission
b Emission for 254 nm excitation

PL emission and excitation result of $\text{NaCe}(\text{PO}_3)_4:0.1\%\text{Dy}$

Figure 3 below shows Emission spectrum of 0.1% Dy doped $\text{NaCe}(\text{PO}_3)_4$. There is significant increase in the emission intensity in the range of $500\text{-}600\text{ nm}$ showing transfer of energy from Ce^{3+} to Dy^{3+} . For 0.1% doping, Ce^{3+} and Dy^{3+} emission is at $\lambda_{\text{ext.}} = 254\text{ nm}$ (curve a). The excitation spectrum for 325 nm emission (curve a) shows very broad band peaking at 236 nm (21989 cm^{-1} , 5.66 eV), 269 nm (25063 cm^{-1} , 6.45 eV), 295 nm (27486 cm^{-1} , 7.07 eV) . The transfer of energy from Ce^{3+} (curve b) to Dy^{3+} (curve c) ions in $\text{NaCe}(\text{PO}_3)_4$ lattice brings Ce^{3+} to the ground state and Dy^{3+} to the excited state. The emission in Dy^{3+} comes via a non- radiative transition to the $^4\text{F}_{9/2}$ level, followed by radiative transitions to $^6\text{H}_{15/2}$ and $^6\text{H}_{13/2}$ levels. Dy^{3+} emission falls mainly in two lines in the visible region arising from $^4\text{F}_{9/2} \rightarrow ^6\text{H}_{15/2}$ ($470\text{-}500\text{ nm}$) and $^4\text{F}_{9/2} \rightarrow ^6\text{H}_{13/2}$ (570 nm) transitions.

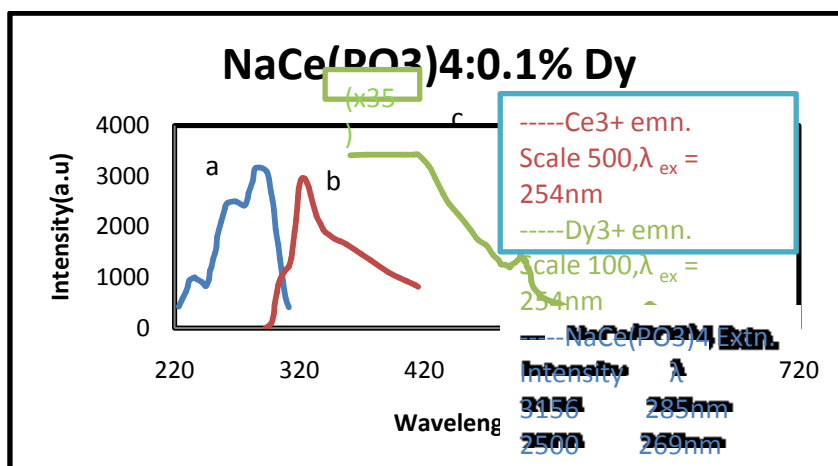


Figure3: PL of $\text{NaCe}(\text{PO}_3)_4:\text{Dy}$

CONCLUSIONS: The metaphosphates $\text{NaCe}(\text{PO}_3)_4$ and $\text{NaCe}(\text{PO}_3)_4:\text{Dy}$ have been successfully prepared. XRD of the synthesized compound matched excellently with the corresponding ICDD data files. Dy^{3+} emission falls mainly in two lines in the visible region arising from $^4\text{F}_{9/2} \rightarrow ^6\text{H}_{15/2}$ (470 -500 nm) and $^4\text{F}_{9/2} \rightarrow ^6\text{H}_{13/2}$ (570 nm) transitions. Energy transfer phenomena have led to the development of new and efficient photoluminescence materials. These phosphors may be applicable in scintillation applications and in the lamp industry.

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