Study of Characterization and Energy Transfer Mechanism in NaCe(PO₄)₄ doped with Rare Earth ions (Dy³⁺, Tb³⁺, Yb³⁺ and Nd³⁺)

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Abstract - NaCe(PO₄)₄ doped with Dy³⁺, Tb³⁺, Yb³⁺ and Nd³⁺ phosphors were synthesized by high temperature solid state diffusion method. The samples were characterized by X-Ray diffraction and photoluminescence. NaCe(PO₄)₄ exhibits emission in UV region. This indicates weak Ce³⁺ - Ce³⁺ interaction. Ce³⁺ - Ce³⁺ energy transfer is not efficient. Energy transfer from Ce³⁺ to other lanthanides like Dy³⁺, Tb³⁺, Yb³⁺ and Nd³⁺ is a surprising result.

KeyWords: Cerium Metaphosphate, XRD, Photo luminescence, High temperature Solid State Synthesis, Energy Transfer

1. INTRODUCTION

The luminescence properties of rare earth-doped phosphate materials have been largely investigated due to the fact that light emission from ultraviolet to far-infrared regions is because of varied optical energy level structures of the rare earth elements [1–3]. Rare earth ortho- and metaphosphates are the class of compounds that have gained much attention due to their luminescence properties. Increasing interest in these materials has been observed since binary and ternary phosphates could be used as laser devices in the form of single crystals, powder and glass [4]. Also, they exhibit good chemical and thermal stability and have a good optical efficiency. In the alkali metal-rare earth phosphate system, the varied combinations of PO₄ groups give rise to the several structural families such as MLnPO₄, M₂Ln(PO₄)₂ and MLn(PO₄)₃ (M = alkali metal, Ln = rare earth metal) etc. Solid-state polyphosphates with the general formula MLn(PO₄)₄ (M = alkali metal, Ln = rare earth metal) are promising functional materials for optical applications [5–9]. From a structural point of view, these materials can be classified in two types: I — the cyclic structure, in which the polyphosphate anion consists in a ring of four PO₄ tetraedra linked by bridging oxygens; II — the chain structure, in which the four PO₄ tetraedra form an elongated chain. Polyphosphates of MLn(PO₄)₄ formula have found to be rare-earths sensitizers—activator pairs, containing phosphors for the energy up conversion [10].

In general, the emission mechanism of rare-earth ion is dependent on large number of factors such as the relative energy of the 4f emitting level, site occupation and guest-host interactions. The absorption edge of the phosphate anion lies at about 60,000 cm⁻¹ (165 nm), which proves that these materials efficiently absorb the VUV energy [11–16]. There are not many studies on luminescence of these compounds although rare earth ions possess interesting luminescence properties which is rather surprising. Amongst rare earth ions, Ce³⁺ exhibits rather peculiar emission which is in form of a two humped broad band, due to split ground state [17,18]. Ce³⁺ exhibits intense emission [19,20] due to allowed electric dipole transitions corresponding to transitions from levels of 5d¹ configuration to 4f states of 4f¹ configuration with fast decay time of the order of several nano seconds. Quenching usually occurs at high concentrations [21] barring some exceptions like YAG:Ce. Many, but not all, stochiometric cerium compounds exhibit strong luminescence. E.g. CePO₄ shows intense emission with a quantum efficiency of 40% [22]. CeF₃, CeO₂ are other examples [21]. Even some hydrated salts of cerium show strong emission [23,24]. On the other hand CeAl₂O₄ does not fluoresce. Concentration quenching occurs due to energy transfer between similar ions and finally to a killer site. Energy transfer from Ce³⁺ to Ce³⁺ has been considered by Boldten [25] and Blase [26–28] and occurs over distance of 15–20 Å. The emission and absorption transitions of Ce³⁺ are allowed as electric dipole transitions. Energy transfer is therefore expected to be proportional to R⁶ [29], where R is the Ce³⁺ - Ce³⁺ distance.

In this paper we report synthesis and photoluminescence of metaphosphate NaCe(PO₄)₄. Various energy transfer processes Ce³⁺ → Tb³⁺, Ce³⁺ → Dy³⁺, Ce³⁺ → Yb³⁺ and Ce³⁺ → Nd³⁺ were studied.

2. EXPERIMENTAL

The polycrystalline samples were prepared using high temperature solid-state reaction technique described by Szczygiel et al. [30] using analytical reagent grade CeO₂, NH₄H₂PO₄ and NaPO₃. For doping, the corresponding salts of the activators were added in desired quantities. The reagents were taken in appropriate stoichiometric ratio and grounded in agate mortar. Sodium meta phosphate NaPO₃ was obtained by complete dehydration of NaH₂PO₃·H₂O at 500°C for 2 hr. Cerium meta phosphate Ce(PO₄)₃ was obtained from cerium oxide CeO₂ and NH₄H₂PO₄ by sintering the mixture of these compounds stochiometrically at 250, 500, and 900°C for 2, 5, and 15 hrs, respectively [31]. NaCe(PO₄)₃ has been obtained from NaPO₃ and Ce(PO₄)₃ by sintering a stoichiometric mixture of these compounds at 750°C for 20 hrs assuming the reaction.

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\text{Ce(PO}_{4})_{3} + \text{NaPO}_{3} \rightarrow \text{NaCe(PO}_{4})_{4}
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After heating as given above, the furnace was slowly cooled down to the room temperature. The resultant polycrystalline mass was crushed to fine particle in a crucible and subjected to XRD and PL 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 width of 1.5 nm. Photoluminescence (PL) spectra in the spectral range above 700 nm were recorded on Photon Technology International QM-51 NIR Spectro-fluorimeter.

3. RESULTS AND DISCUSSIONS

Fig-1: XRD patterns of the NaCe(PO₄)₄ compared with JCPDS -33-1233

Fig-1 shows the XRD of prepared NaCe(PO₄)₄. X-ray diffraction of prepared NaCe(PO₄)₄ is found to match with ICDD file 33-1233 of NaCe(PO₄)₄. NaCe(PO₄)₄ belongs to type III structures among seven types mentioned by Palkina et al[32]. According to Zhu et al[33], NaCe(PO₄)₄ is monoclinic with the P2₁/m(C2h) unit cell.

Fig-2(a&b): Coordination of Anions

Fig-2(a and b) shows the coordination of anions. The basic structural unit is (PO₄)₄ wavy chain along a-axis, which is composed of corner-sharing PO₄ tetrahedra. Both Ce and Na atoms are connected with eight O atoms. Each PO₄ tetrahedron is linked with the surrounding Ce and Na atoms via sharing two O atoms to build a three-dimensional framework. CeO₆ and NaO₆ polyhedra are alternately arranged via face sharing along a-axis and each NaO₆ polyhedron is edge sharing with one CeO₆ polyhedron along b-axis. Three CeO₆ and three NaO₆ polyhedra delimit an infinite tunnel along c-axis.

The emission spectra given in Fig.3(curve a) shows intense PL emission with two peaks at 346 nm(28901 cm⁻¹, 3.59 eV) and 327.6 nm(30525 cm⁻¹, 3.79 eV) upon 254 nm excitation for NaCe(PO₄)₄. These are due to transitions from the lowest level of 5d configuration to the ⁴F₇/₂, ⁴F₅/₂ states of the 4f³ configuration in Ce³⁺ ions. There are also two half intensity peaks at 316 nm(31645 cm⁻¹, 3.94 eV) and 361 nm(27701 cm⁻¹, 3.44 eV). The PL excitation spectrum at 346nm emission (Fig.3, curve b) shows a broad band in the range 220 nm to 320 nm with peak at 298.6 nm (33489 cm⁻¹, 3.16 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, 4.4 eV) and 282 nm(35461 cm⁻¹, 4.40 eV). From these results, the Stokes shift amounts to be about (2964 cm⁻¹).

It is thus seen that there is no strong concentration quenching in NaCe(PO₄)₄ and energy transfer among Ce³⁺ ions is very weak. This is consistent with the observation of Zhu et al[33] that “CeO₆ polyhedral are isolated from each other, and the shortest Ce–Ce distance is 6.210 Å. This possibly causes the decreased interaction of Ce–Ce and a decreased concentration fluorescence quenching may be predicted”. Weak energy transfer among Ce³⁺ ions may suggest that Ce³⁺ will not act as sensitizer. On the other hand, strong Ce³⁺ → Tb³⁺ transfer has been observed in CeMgAl₁₂O₁₉ [34,35] despite such weak Ce–Ce interaction. We thus decided to study such energy transfers among Ce³⁺ and other rare earth ions in NaCe(PO₄)₄ host.

3.1 Ce³⁺ → Dy³⁺ energy transfer

Dy³⁺ emission falls mainly in two lines in the visible region arising from ⁴F₇/₂ → ⁶H₅/₂ (470-500 nm) and ⁴F₅/₂ → ⁶H₇/₂ (570 nm) transitions. The relative intensities of the two bands depend on the local symmetry[34]. When the ratio of blue to yellow emission is appropriated, one can obtain white emission using Dy³⁺. This property has generated some interest in Dy³⁺ luminescence. UV cannot efficiently excite Dy³⁺ because its CT state as well as the 5d levels are situated well above 50,000 cm⁻¹. Dy³⁺ can be sensitized by Bi³⁺ [35], Gd³⁺, Ce³⁺, Pb²⁺ and Vanadate[36-38]ions. Gadolinium alumino-borate (GdAl₃B₄O₁₂) doped...
with Bi$^{3+}$ and Dy$^{3+}$ is an efficient lamp phosphor. Bismuth absorbs UV energy and transfers to Gd. The energy migrates in Gd sub-lattice and is finally transferred to Dy$^{3+}$. YVO$_5$:Dy$^{3+}$ is another lamp phosphor. Dy doped phosphors are also useful in dosimetry of ionizing radiation using thermoluminescence. CaSO$_4$:Dy, CaF$_2$:Dy, MgB$_2$O$_4$:Dy are some of the phosphors [39] used in personnel monitoring using thermoluminescence dosimetry.

![Excitation and emission spectra NaCe(PO$_4$)$_3$ :Dy(0.1%, 0.5%and 1%)](Image)

Excitation spectra for 1%Dy$^{3+}$ (for 481 nm Emission) Emission spectra of Dy$^{3+}$ (for 285 nm Excitation), Dy$^{3+}$ concentrations

(a) 0.1% (b) 0.5% (c) 1%

(e) Excitation for 330 nm (Ce$^{3+}$) emission

(f) Ce$^{3+}$ emission for 285 nm excitation

For Dy doping in NaCe(PO$_4$)$_3$, the PL curves are shown in Fig. 4(a-f). Two very intense and sharp peaks at 477 and 574 nm are obtained in emission spectra for Dy$^{3+}$ as shown in Fig. 4(b-d) for 285 nm excitation. These correspond to $^4$F$_{9/2}$ $\rightarrow$ $^4$H$_{15/2}$ and $^4$F$_{9/2}$ $\rightarrow$ $^4$H$_{13/2}$ transitions of Dy$^{3+}$. The broad band around 330 nm is due to Ce$^{3+}$. The excitation spectrum for 1% Dy$^{3+}$ (curve a) shows the broad band in UV region around 270 nm with shoulders on either side around 250 and 331 nm. These shoulders coincide with the excitation bands observed for the Ce$^{3+}$ 338 nm emission (curve e). In addition, there are weak lines around 368 and 384 nm which correspond to transitions $^4$H$_{15/2}$ $\rightarrow$ $^4$I$_{11/2}$ and $^4$H$_{15/2}$ $\rightarrow$ $^4$I$_{13/2}$ respectively. Curve (f) is emission spectra for Ce$^{3+}$ for 285 nm excitation. Ce$^{3+}$ emission peak at 345 nm overlaps with the f-excitation lines for Dy$^{3+}$. Hence, energy transfer is seen from Ce$^{3+}$ to Dy$^{3+}$ ions. Also The Dy$^{3+}$ emission was studied for various concentrations (Fig. 4, curves b-d). The emission intensities increase with increasing concentration. The highest intensity was observed for 0.5% Dy$^{3+}$. Concentration quenching was observed for higher concentrations. The concentration quenching mechanism is generally associated with energy transfer.

![Fig-5:Ce$^{3+}$to Dy$^{3+}$ energy transfer diagram](Image)

The transfer of energy from Ce$^{3+}$ to Dy$^{3+}$ ions in the NaCe(PO$_4$)$_3$ 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 $^4$F$_{9/2}$ level, followed by radiative transitions to $^6$H$_{15/2}$ and $^6$H$_{13/2}$ level, which is shown in Figure 5. It is known that Dy$^{3+}$ emission around 486 nm ($^4$F$_{9/2}$ $\rightarrow$ $^4$H$_{15/2}$) is of magnetic dipole origin and 576 nm ($^4$F$_{9/2}$ $\rightarrow$ $^4$H$_{13/2}$) is of electric dipole origin. $^4$F$_{9/2}$ $\rightarrow$ $^6$H$_{13/2}$ is predominant only when Dy$^{3+}$ ions are located at low symmetry sites with no inversion centres [40].

### 3.2 Ce$^{3+}$ $\rightarrow$ Tb$^{3+}$ energy transfer

The ground states ($4f^5$) of Tb$^{3+}$ are $^7$F configurations, when one electron is promoted to 5d shell, it can give rise to two $4f^65d^1$ excitation states: the high-spin states with $^7$D$_1$ configurations or low-spin states with $^7$D$_2$ configurations. Obviously, $^7$D$_1$ states will be lower in energy according to Hund’s rule, and the transitions between $^7$F$_J$ and $^7$D$_J$ are spin-allowed, while $^7$F$_J$ $\rightarrow$ $^7$D$_J$ transitions are spin-forbidden. Therefore, the spin-allowed f–d transitions are strong, with higher energy; the spin-forbidden f–d transitions are weak, with lower energy. Terbium shows strong excitation corresponding to allowed transitions between $^7$F$_{6}$ ground state of 4f$^6$ configuration to the levels of 4f$^5$5d$^1$ configuration which falls in deep UV or VUV region of the spectrum. From the excited state the ion relaxes in several steps to $^7$D$_J$ levels of 4f$^5$ configuration. Line emission corresponding to f–f transitions is observed. Commonly observed most intense lines are around 487 nm and 542 nm corresponding to $^7$D$_{2}$ $\rightarrow$ $^7$F$_{5}$ and $^7$D$_{2}$ $\rightarrow$ $^7$F$_{6}$ transitions, respectively. At low concentrations blue emission is dominant. Near UV emission around 385 nm corresponding to $^7$D$_{2}$ $\rightarrow$ $^7$F$_{5}$ transition is also observable. For high concentrations, these emissions are quenched by cross relaxation relaxation from the $^7$D$_{2}$ to the $^7$D$_{3}$ state and multiphonon relaxation occurring in host lattices with high phonon frequency and the green emission becomes dominant.
Concentration quenching was observed for higher Tb concentrations. The highest intensity was observed for 0.5% Tb doping (curve d). The emission intensity for 1% (Curve b) and 5% (Curve c) Tb doping (curve d) compared to that is obtained for 10% Tb doping (Curve e). It contains a strong Ce³⁺ emission peak around 331 nm, and only weak lines of Tb³⁺. There is clear increase in luminescence intensity for 1% Tb doping (Curve b) and 5% Tb doping (Curve c) compared to that is obtained for 10% Tb doping (Curve d). The excitation spectrum for 311 nm Ce³⁺ emission (Curve e) shows very broad bands peaking at 238, 264 nm and 303 nm. Curve (a) which corresponds to Tb³⁺ excitation also contains these bands, thus showing a clear Ce³⁺ → Tb³⁺ energy transfer. Additional peaks in curve (a) around 285 and 311 nm may be assigned to allowed transitions between 7F₅ ground state of 4f³ configuration to the levels of 4F₅d¹ configuration. The Tb³⁺ emission was studied for various concentrations (Fig. 6, curves b-d). The emission intensities increase with increasing concentration. The highest intensity was observed for 0.5% Tb³⁺. Concentration quenching was observed for higher concentrations. Fig. 7 explains the Ce³⁺ → Tb³⁺ energy transfer.
Excitation spectra for 1%Yb³⁺(for 980 nm emission), Yb³⁺ concentrations
(a) 1%  (b) 5%  (c) 10%
Emission spectra of Yb³⁺ (for 304nm Excitation), Yb³⁺ concentrations
(d) 1%  (e) 5%  (f) 10%

Fig.9 explains the mechanism. Ce³⁺ absorbs a high energy photon using allowed 4f-5d transitions. The energy is then transferred to two Yb³⁺ ions which emit two NIR photons[44]. Thus Energy transfer occurs from Ce³⁺to Yb³⁺ in KCe(PO₄)₃, but the efficiency is very low.

3.4Ce³⁺ → Nd³⁺ energy transfer

Using Luminescent materials, one method of improving efficiency of photovoltaic devices is developed by modifying solar spectrum. Developing such an technique can eliminate the spectral mismatch phenomenon greatly by improving the utilization of sunlight. This leads indirectly in improving the efficiency and performance of solar cell [45]. Rare earth ions like Yb³⁺ or Nd³⁺ along with other lanthanides or transition metals doped in inorganic materials can be used as spectral conversion, as they emit in the region where there is high spectral response of c-Si solar cell. There are many reports on near infrared emitting phosphors via downshifting, downconversion or upconversion process [46–53].

The Emission and Excitation spectra of Nd³⁺ doped NaCe(PO₄)₃ with varying Nd concentration from 1to10 mol% are shown in Fig.10(a–h). Curve (a) shows Excitation spectrum for 5% Nd (for 1054nm Emission) consisting of several lines in the range 220–800 nm corresponding to various f–f transitions of Nd³⁺ ions. Some prominent transitions are 4I9/2→4I9/2 (361nm), 4I9/2→4F1/2 (435 nm), 4I9/2→4G11/2 (468nm), 4I9/2→4F9/2 (479nm), 4I9/2→4G7/2, 4G5/2 (526, 514 nm), 4I9/2→4G9/2, 4G7/2, 2H11/2(around 583 nm), 4I9/2→4H11/2 (629 nm), 4I9/2→4F9/2 (686nm), 4I9/2→4F7/2, 4S9/2 (748,736nm) and 4I9/2→4F5/2, 4F3/2 (824, 808 nm)[54–56].Intense characteristic emission of Nd³⁺at 889nm,1054nm and 1330nm assigned to the 4F5/2 to 4I11/2 and 4I13/2 transitions of Nd³⁺ were observed under 304nm excitation in curve(d). The Nd³⁺ emission was studied for various concentrations (Fig.10,curves b–e). The emission intensities increase with increasing concentration. The highest intensity was observed for 0.5% Nd³+. Concentration quenching was observed for higher concentrations. In Fig.10, the Ce³⁺ emission spectrum(curve f) at 254nm excitation overlaps well with sharp excitation peaks of Nd³+(curve a) at 352nm, 357nm and 423nm, which suggests the possibility of Energy transfer from Ce³⁺ to Nd³⁺ ions. Fig.11 explains the Ce³⁺- Nd³⁺ Energy Transfer.
4. CONCLUSIONS
Stoichiometric cerium compound NaCe(PO₃)₄ exhibits intense photoluminescence indicating weak Ce³⁺ - Ce³⁺ interaction. This is expected as the shortest Ce–Ce distance is 6.6210 Å. It may be speculated that the energy transfers take place between neighbouring Ce³⁺ and rare earth ions, which does not involve energy migration over Ce³⁺ sublattice.

ACKNOWLEDGEMENT
We are thankful to I.C.M.R, New Delhi and Board of Research in Nuclear Sciences (BRNS), Department of Atomic Energy, Govt. of India, for providing financial assistance to carry out this work.

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