

Study of Characterization and Energy Transfer Mechanism in NaCe(PO₃)₄ doped with Rare Earth ions (Dy³⁺, Tb³⁺, Yb³⁺ and Nd³⁺)

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Abstract - NaCe(PO₃)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(PO₃)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

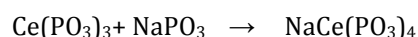
The luminescence properties of rare earth-doped phosphate materials have been largely investigated due to the fact that light emission from ultraviolet to far-infrared regions is because of varied optical energy level structures of the rare earth elements. [1-3] Rare earth ortho- and metaphosphates are 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 MLnP₂O₇, M₃Ln(PO₄)₂ and MLn(PO₃)₄ (M = alkali metal, Ln = rare earth metal) etc. Solid-state polyphosphates with the general formula MLn(PO₃)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 tetrahedra linked by bridging oxygens; II—a chain structure, in which the four PO₄ tetrahedra form an elongated chain. Polyphosphates of MLn(PO₃)₄ formula have found to be rare-earths sensitizer-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 ²F_J 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, stoichiometric cerium compounds exhibit strong luminescence. e.g. CePO₄ shows intense emission with a quantum efficiency of 40% [22]. CeF₃, CeBO₃ are other examples [21]. Even some hydrated salts of cerium show strong emission [23,24]. On the other hand CeAlO₃ 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 Boltzen [25] and Blasse [26-28] and occurs over distance of 15-20 Å⁰. The emission and absorption transitions of Ce³⁺ are allowed as electric dipole transitions. Energy transfer is therefore expected to be proportional to R⁻⁶ [29], where R is the Ce³⁺- Ce³⁺ distance.

In this paper we report synthesis and photoluminescence of metaphosphate NaCe(PO₃)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 NaH₂PO₄.H₂O at 500°C for 2hr. Cerium meta phosphate Ce(PO₃)₃ was obtained from cerium oxide CeO₂ and NH₄H₂PO₄ by sintering the mixture of these compounds stoichiometrically at 250, 500, and 900°C for 2, 5, and 15 hrs., respectively [31]. NaCe(PO₃)₄ has been obtained from NaPO₃ and Ce(PO₃)₃ by sintering a stoichiometric mixture of these compounds at 750°C for 20 hrs assuming the reaction.



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

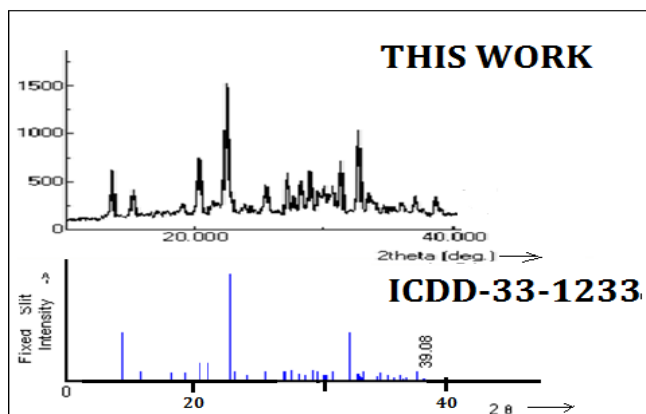


Fig -1: XRD patterns of the NaCe(PO₃)₄ compared with JCPDS -33-1233

Fig-1 shows the XRD of prepared NaCe(PO₃)₄. X-ray diffraction of prepared NaCe(PO₃)₄ is found to match with ICDD file 33-1233 of NaCe(PO₃)₄. NaCe(PO₃)₄ belongs to type III structures among seven types mentioned by Palkina et al [32]. According to Zhu et al [33], NaCe(PO₃)₄ is monoclinic with the P2₁/m(C_{2h}²) unit cell.

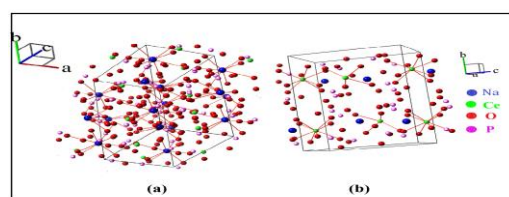


Fig -2(a&b): Coordination of Anions

Fig-2(a and b) shows the coordination of anions. The basic structural unit is (PO₃)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. CeO₈ and NaO₈ polyhedra are alternately arranged via face sharing along a-axis and each NaO₈ polyhedron is edge sharing with one CeO₈ polyhedron along b-axis. Three CeO₈ and three NaO₈ polyhedra delimit an infinite tunnel along c-axis.

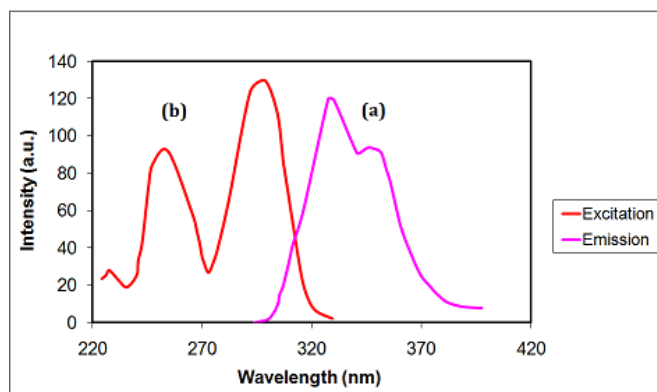


Fig -3: PL and PLE spectra of NaCe(PO₃)₄
(a) Emission for 254 nm excitation
(b) Excitation for 344 nm emission

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(PO₃)₄. These are due to transitions from the lowest level of 5d configuration to the ²F_{5/2}, ²F_{7/2} states of the 4f¹ 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 346 nm 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, 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 be about (2964 cm⁻¹).

It is thus seen that there is no strong concentration quenching in NaCe(PO₃)₄ and energy transfer among Ce³⁺ ions is very weak. This is consistent with the observation of Zhu et al [33] that "CeO₈ polyhedra 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 CeMgAl₁₁O₁₉ [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(PO₃)₄ host.

3.1 Ce³⁺ → Dy³⁺ energy transfer

Dy³⁺ emission falls mainly in two lines in the visible region arising from ⁴F_{9/2} → ⁶H_{15/2} (470 -500 nm) and ⁴F_{9/2} → ⁶H_{13/2} (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 appropriate, 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 Bi³⁺ and Dy³⁺ 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 Dy³⁺. YVO₄:Dy³⁺ is another lamp phosphor. Dy doped phosphors are also useful in dosimetry of ionizing radiation using thermoluminescence. CaSO₄:Dy, CaF₂:Dy, MgB₄O₇:Dy are some of the phosphors [39] used in personnel monitoring using thermoluminescence dosimetry.

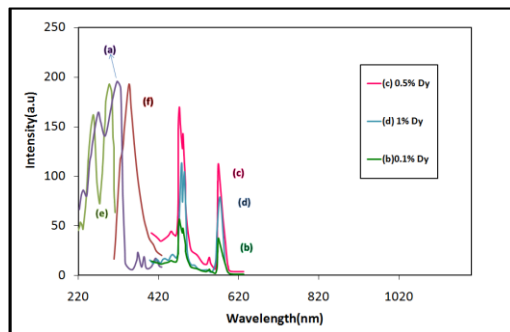


Fig-4: Excitation and emission spectra NaCe(PO₃)₄:Dy(0.1%, 0.5% and 1%)
 Excitation spectra for 1% Dy³⁺ (for 481 nm Emission)
 Emission spectra of Dy³⁺ (for 285 nm Excitation), Dy³⁺ concentrations
 (b) 0.1% (c) 0.5% (d) 1%
 (e) Excitation for 330 nm (Ce³⁺) emission
 (f) Ce³⁺ emission for 285 nm excitation

For Dy doping in NaCe(PO₃)₄, 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 Dy³⁺ as shown in Fig. 4(b-d) for 285 nm excitation. These correspond to ⁴F_{9/2} → ⁶H_{15/2} and ⁴F_{9/2} → ⁶H_{13/2} transitions of Dy³⁺. The broad band around 330 nm is due to Ce³⁺. The excitation spectrum for 1% Dy³⁺ (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 Ce³⁺ 338 nm emission (curve e). In addition, there are weak lines around 368 and 384 nm which correspond to transitions ⁶H_{15/2} → ⁶I_{11/2} and ⁶H_{15/2} → ⁴I_{13/2}, respectively. Curve (f) is emission spectra for Ce³⁺ for 285 nm excitation. Ce³⁺ emission peak at 345 nm overlaps with the f-f excitation lines for Dy³⁺. Hence, energy transfer is seen from Ce³⁺ to Dy³⁺ ions. Also The Dy³⁺ 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% Dy³⁺. Concentration quenching was observed for higher concentrations. The concentration quenching mechanism is generally associated with energy transfer.

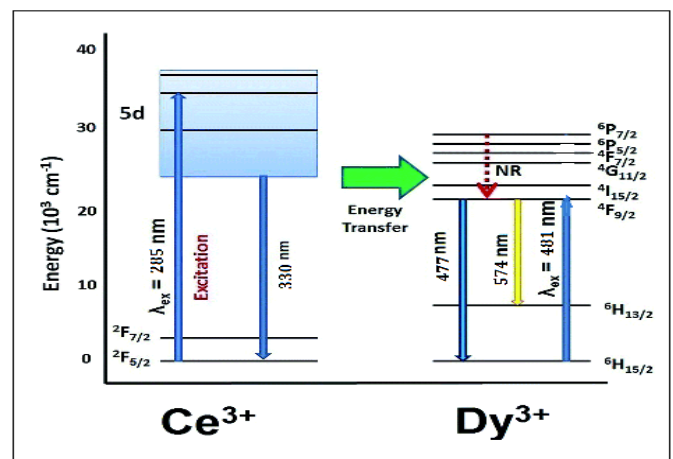


Fig-5: Ce³⁺ to Dy³⁺ energy transfer diagram

The transfer of energy from Ce³⁺ to Dy³⁺ ions in the NaCe(PO₃)₄ lattice brings Ce³⁺ to the ground state and Dy³⁺ to the excited state. The emission in Dy³⁺ comes via a non-radiative transition to the ⁴F_{9/2} level, followed by radiative transitions to ⁶H_{15/2} and ⁶H_{13/2} level, which is shown in Figure 5. It is known that Dy³⁺ emission around 486 nm (⁴F_{9/2} → ⁶H_{15/2}) is of magnetic dipole origin and 576 nm (⁴F_{9/2} → ⁶H_{13/2}) is of electric dipole origin. ⁴F_{9/2} → ⁶H_{13/2} is predominant only when Dy³⁺ ions are located at low symmetry sites with no inversion centres [40].

3.2 Ce³⁺ → Tb³⁺ energy transfer

The ground states (4f⁸) of Tb³⁺ are ⁷F_J configurations, when one electron is promoted to 5d shell, it can give rise to two 4f⁷5d¹ excitation states: the high-spin states with ⁹D_J configurations or low-spin states with ⁷D_J configurations. Obviously, ⁹D_J states will be lower in energy according to Hund's rule, and the transitions between ⁷F_J and ⁷D_J are spin-allowed, while ⁷F_J → ⁹D_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 ⁷F₆ ground state of 4f⁸ configuration to the levels of 4f⁷5d¹ configuration which falls in deep UV or VUV region of the spectrum. From the excited state the ion relaxes in several steps to ⁵D_J levels of 4f⁸ configuration. Line emission corresponding to f-f transitions is observed. Commonly observed most intense lines are around 487 nm and 542 nm corresponding to ⁵D₄ → ⁷F₅ and ⁵D₄ → ⁷F₆ transitions, respectively. At low concentrations blue emission is dominant. Near UV emission around 385 nm corresponding to ⁵D₃ → ⁷F₆ transition is also observable. For high concentrations, these emissions are quenched by cross relaxation relaxation from the ⁵D₃ to the ⁷D_J state and multiphonon relaxation occurring in host lattices with high phonon frequency and the green emission becomes dominant.

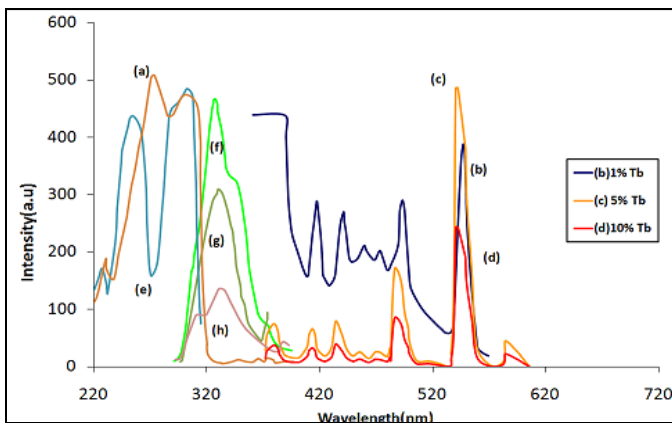


Fig-6: $Ce^{3+} \rightarrow Tb^{3+}$ energy transfer in $NaCe(PO_3)_4:Tb^{3+}$ Excitation and emission spectra $Na(PO_3)_4 :Tb(1\%, 5\% \text{ and } 10\%)$

- (a) Excitation for 543 nm (Tb^{3+} , 5 %) emission
- Emission spectra of Tb^{3+} (for 285nm Excitation), Tb^{3+} concentrations
- (b) 1% (c) 5% (d) 10%
- (e) Excitation for 331 nm (Ce^{3+}) emission
- Emission spectra of Ce^{3+} (for 254nm Excitation), Tb^{3+} concentrations
- (f) 1% (g) 5% (h) 10%

Excitation and emission spectra of $NaCePO_4:Tb(1\%, 5\%, 10\%)$ are as shown in Fig. 6. Curve (a) shows excitation spectrum for 5% Tb doping for emission at 543 nm. It contains several overlapping bands around 238, 264, 285, 303 and 311 nm. In emission spectra (for 285nm Excitation) (Curves b-d) intensity peaks are observed at 474, 488, 549 and 585 nm which correspond to ${}^5D_4 \rightarrow {}^7F_J$, $J=6, 5, 4, 3$ transitions of Tb^{3+} respectively. Intensity peaks observed at 379.6nm, 414nm, 435 nm and 456 nm correspond to transitions ${}^5D_3 \rightarrow {}^7F_J$, $J=6, 5, 4, 3$. Curve (b) shows emission spectra at 285 nm excitation for the sample containing 1 % Tb. It contains a strong Ce^{3+} emission peak around 331 nm, and only weak lines of Tb^{3+} . There is clear increase in luminescence intensity for 1%(Curve b) and 5% doping(Curve c) compared to that is obtained for 10% doping(curve d). The excitation spectrum for 331 nm Ce^{3+} emission (curve e) shows very broad bands peaking at 238, 264 nm and 303 nm. Curve (a) which corresponds to Tb^{3+} excitation also contains these bands, thus showing a clear $Ce^{3+} \rightarrow Tb^{3+}$ energy transfer. Additional peaks in curve (a) around 285 and 311 nm may be assigned to allowed transitions between 7F_6 ground state of $4f^8$ configuration to the levels of $4f^75d^1$ configuration. The Tb^{3+} 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% Tb^{3+} . Concentration quenching was observed for higher concentrations. Fig.7 explains the $Ce^{3+} \rightarrow Tb^{3+}$ energy transfer

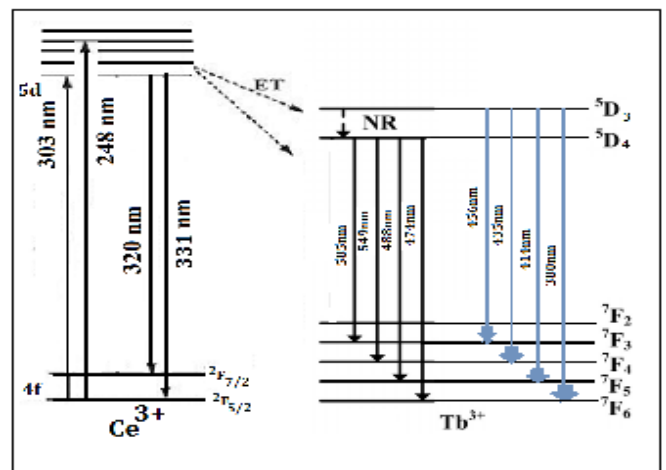


Fig-7: Ce^{3+} to Tb^{3+} energy transfer diagram

3.3 $Ce^{3+} \rightarrow Yb^{3+}$ energy transfer

In recent years $Ce^{3+} \rightarrow Yb^{3+}$ energy transfer has become important for down converting the solar spectrum [41-43] so as to match the c-Si solar cell response which is maximum around 1000 nm, band gap of Si being around 1.1 eV. Yb^{3+} has only two energy levels which are separated by almost same energy. However, f-f excitations of Yb^{3+} are very weak due to forbidden nature of such transitions. Ce^{3+} excitation, on the other hand, arising from allowed f-d transitions, are very strong. In suitable host, Ce^{3+} can efficiently absorb near UV/ blue light and cause quantum cutting through cooperative energy transfer to two Yb^{3+} ions. We studied $Ce^{3+} \rightarrow Yb^{3+}$ energy transfer in $NaCe(PO_3)_4:Yb$ with this view.

Excitation and emission spectra of $NaCe(PO_3)_4:Yb(1\%, 5\%, 10\%)$ are as shown in Fig. 8. Curve a shows excitation spectrum for 1% Yb^{3+} for emission at 980 nm. A distinct band is seen around 304 nm which is almost same as that for Ce^{3+} excitation. Curves b-d show emission for 304 nm excitation. As the concentration of Yb^{3+} ions increases, the emission intensity of Ce^{3+} remarkably decreases and the NIR emission intensity of Yb^{3+} ions initially increases and then decreases due to concentration quenching (curves b, c and d). Cooperative Energy transfer (CET mechanism) takes place from Ce^{3+} to Yb^{3+} ions.

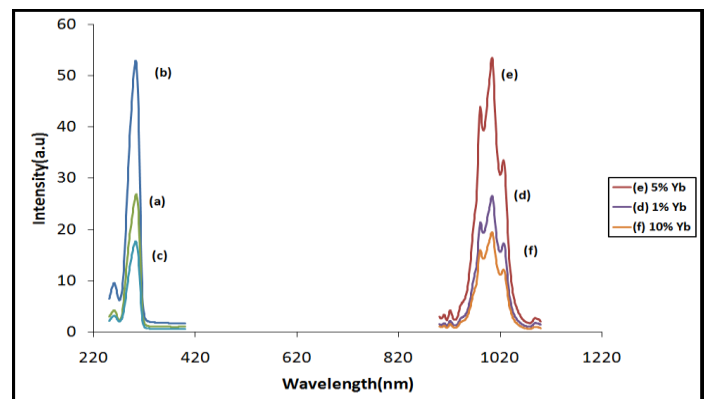


Fig-8: Excitation and emission spectra $NaCe(PO_3)_4$

:Yb(1%, 5% and 10%)

Excitation spectra for 1% Yb³⁺ (for 980 nm emission), Yb³⁺ concentrations

(a) 1% (b) 5% (c) 10%

Emission spectra of Yb³⁺ (for 304 nm 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(PO₃)₄, but the efficiency is very low.

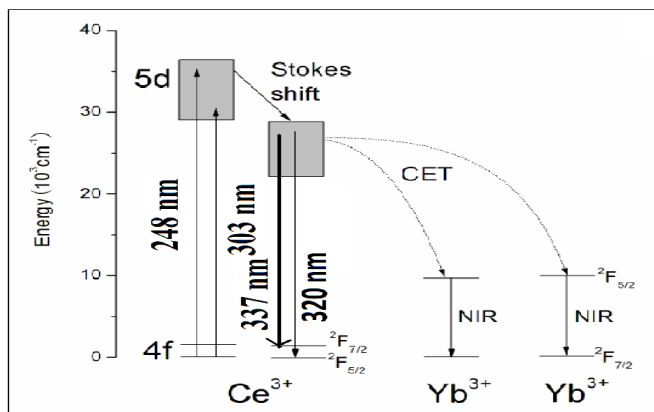


Fig-9: Ce³⁺ to Yb³⁺ energy transfer diagram

3.4 Ce³⁺ → Nd³⁺ energy transfer

Using Luminescent materials, one method of improving efficiency of photovoltaic devices is developed by modifying solar spectrum. Developing such a 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].

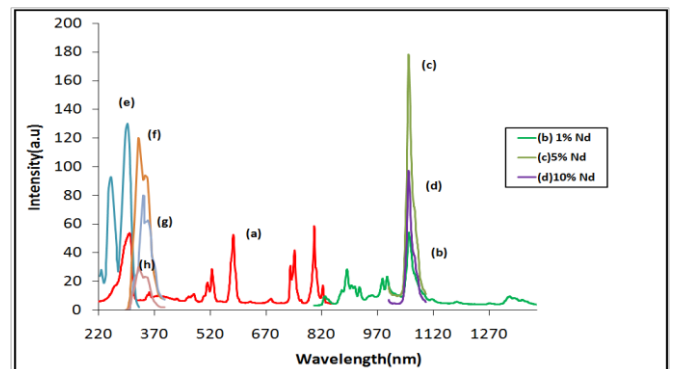


Fig-10: Excitation and emission spectra NaCe(PO₃)₄:Nd(1%, 5%, 10%)

(a) Excitation spectra for 5% Nd³⁺ (for 1054 nm Emission)

Emission spectra of Nd³⁺ (for 304 nm Excitation), Nd³⁺ concentrations

(b) 1% (c) 5% (d) 10%

(e) Excitation for 338 nm (Ce³⁺) emission

Emission spectra of Ce³⁺ (for 254 nm Excitation), Nd³⁺ concentrations

(f) 1% (g) 5% (h) 10%

The Emission and Excitation spectra of Nd³⁺ doped NaCe(PO₃)₄ with varying Nd concentration from 1 to 10 mol% are shown in Fig.10(a-h). Curve (a) shows Excitation spectrum for 5% Nd (for 1054 nm Emission) consisting of several lines in the range 220-800 nm corresponding to various f-f transitions of Nd³⁺ ions. Some prominent transitions are ⁴I_{9/2} → ⁴D_{5/2} (361 nm), ⁴I_{9/2} → ²P_{1/2} (435 nm), ⁴I_{9/2} → ⁴G_{11/2} (468 nm), ⁴I_{9/2} → ⁴G_{9/2} (479 nm), ⁴I_{9/2} → ²G_{7/2}, ⁴G_{5/2} (526, 514 nm), ⁴I_{9/2} → ²G_{9/2}, ⁴G_{7/2}, ²H_{11/2} (around 583 nm), ⁴I_{9/2} → ²H_{11/2} (629 nm), ⁴I_{9/2} → ⁴F_{9/2} (686 nm), ⁴I_{9/2} → ⁴F_{7/2}, ⁴S_{3/2} (748, 736 nm) and ⁴I_{9/2} → ²F_{3/2}, ²F_{5/2} (824, 808 nm) [54-56]. Intense characteristic emission of Nd³⁺ at 889 nm, 1054 nm and 1330 nm assigned to the ⁴F_{3/2} to ⁴I_{9/2}, ⁴I_{11/2} and ⁴I_{13/2} transitions of Nd³⁺ were observed under 304 nm 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 254 nm excitation overlaps well with sharp excitation peaks of Nd³⁺ (curve a) at 352 nm, 357 nm and 423 nm, which suggests the possibility of Energy transfer from Ce³⁺ to Nd³⁺ ions. Fig.11 explains the Ce³⁺-Nd³⁺ Energy Transfer.

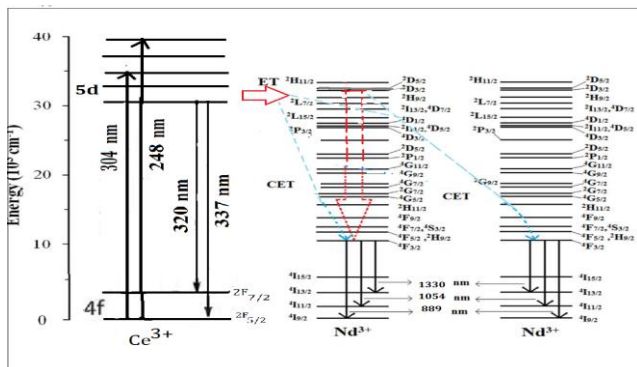


Fig-11: Ce³⁺to Nd³⁺ energy transfer diagram

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 transfer takes place between neighbouring Ce³⁺ and rare earth ions, which does not involve energy migration over Ce³⁺ sublattice.

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