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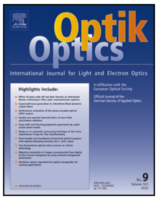

Energy transfer studies in $Ca_{10}Li(PO_4)_7$:Ce^{3+}, Nd^{3+}

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ABSTRACT

During recent years, efficient emission of lanthanide activators in $Ca_{10}Li(PO_4)_7$ host has been reported. Luminescence of rare earth activators such as Ce^{3+}, Dy^{3+}, Sm^{3+} and Ho^{3+}, Er^{3+} has been reported and found suitable for various applications like solid state lighting. Most of these studies are related to visible emission. There are not many reports on NIR emission though it can be important for several applications like bioimaging, telecommunications, solar photovoltaics, Photodynamic therapy, photostimulated localized hyperthermia, etc. Efficient NIR emission in $Ca_{10}Li(PO_4)_7$ host activated with Nd^{3+} is reported in the present work, which could be useful for obtaining Nd^{3+} based phosphors emitting in NIR region. The emission could be sensitized using $Ce^{3+} \rightarrow Nd^{3+}$ energy transfer.

1. Introduction

Double calcium and alkali metal phosphates described by the general formula $Ca_{10}M(PO_4)_7$ [M = Li (I), Na (II), and K (III)] crystallize in the trigonal system and are isostructural to beta-$Ca_3(PO_4)_2$. Morozov et al. described the crystal structures of binary calcium and alkali metal phosphates, $Ca_{10}M(PO_4)_7$ (M = Li, Na, K) in details [1]. Interesting luminescence properties have been reported in these hosts recently. Eu^{2+} emission in $Ca_{10}Na(PO_4)_7$ [2] and $Ca_{10}K(PO_4)_7$ [3] was claimed to be useful for solid state lighting applications. Song et al. [4] studied luminescence of Eu^{3+} in $Ca_{10}Li(PO_4)_7$ host while Zhang et al. [5] reported luminescence of Eu^{2+} which was again found suitable for LED lamps. Chen et al. [6] suggested tuning this emission and extending the excitation beyond nUV region by forming solid solutions. Zhang et al. [7] suggested $Ce^{3+} \rightarrow Mn^{2+}$ energy transfer for obtaining white emission. Luminescence of other rare earth activators such as Ce^{3+}, Dy^{3+} [8], Sm^{3+} [9] and Ho^{3+}, Er^{3+}, and Yb^{3+} [10] has also been reported and found various applications. Most of these studies, except for those on heavy rare earths are related to visible emission. There are not many reports on NIR emission. Recently, we have reported NIR emission in $Ca_{10}Li(PO_4)_7$ host [11]. NIR emission can be important for several applications like bioimaging [12], telecommunications [13], solar photovoltaics [14], Photodynamic therapy [15], photostimulated localized hyperthermia [16] etc.

Among the lanthanide ions, Nd^{3+} is one of the most frequently reported activator which leads to NIR emission. Trivalent neodymium has several technically important luminescent bands based on the transitions $^4F_{3/2} \rightarrow {}^4I_{11/2}$ (the basis of 1067 nm Nd^{3+} lasers), $^4F_{3/2} \rightarrow {}^4I_{9/2}$ (a second lasing transition at ~887 nm), and $^4F_{3/2} \rightarrow {}^4I_{13/2}$ (1350 nm laser channel). NIR luminescence of Nd^{3+} originates from forbidden f–f transitions. These f–f transitions are usually with low direct excitation efficiency (extinction coefficients are typically $1 \times 10^{-10}\ M^{-1}\ cm^{-1}$) and very long lifetime (typically in the range from microseconds to milliseconds). Most common method for getting over this problem is to use a sensitizer. Nd^{3+} has several energy levels spread from near UV region to near infrared through visible. These levels can match the emission of several emitters. By

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virtue of the plethora of these levels, it is possible to sensitize NIR emission of Nd^{3+}. Sensitization of the NIR emission of Nd^{3+} by Ce^{3+} is well known in various phosphors such as YAG:Ce^{3+}, Nd^{3+} [17], $CaSc_2O_4$:Ce^{3+}, Nd^{3+} [18], CaS:Ce^{3+}, Nd^{3+}, SrS:Ce^{3+}, Nd^{3+} [19]. We have also chosen Ce^{3+} as a sensitizer for increasing the intensity of Nd^{3+} emission in $Ca_{10}Li(PO_4)_7$ host. Efficient NIR emission using $Ce^{3+} \rightarrow Nd^{3+}$ energy transfer is reported here.

2. Experimental

A series of samples $Ca_{10(1-x-y)}Li(PO_4)_7$:xCe^{3+}, yNd^{3+}($x = 1–10$ mol%; $y = 0.5–4$ mol%) were synthesized by conventional solid state reaction. Calcium Carbonate ($CaCO_3$), Lithium Carbonate (Li_2CO_3), Ammonium Dihydrogen Phosphate ($NH_4H_2PO_4$), Neodymium oxide (Nd_2O_3) were used as precursors. All the reagents used were of analytical grade. All the precursors were thoroughly mixed and pre-heated at 600 °C for 3 h in air and reduced at 900 °C for 3 h in a reducing atmosphere provided by burning charcoal. The prepared samples were ground to fine powders and taken for further characterizations.

The crystallinity and purity of the prepared samples were examined by measurement on Panalytical X-ray Diffractometer equipped with a copper target (Cu Kα1, $\lambda = 1.5406$ Å). Diffraction data was collected in the range of 10–75° with a step size of 0.017°. The obtained XRD data was refined using Rietveld refinement by Full Prof suite software. Scanning electron micrographs were obtained on Carl Zeiss EVO 18. For recording NIR photoluminescence spectra, Photon Technology International QM-51 NIR Spectro-fluorimeter was used. PL in the visible range was recorded in the range 200–700 nm on Hitachi F 7000 spectrofluorimeter. Reflectance spectra in the visible region were also recorded on the same instrument by choosing "synchronous" mode. $BaSO_4$ was used as standard. Lifetime measurements were carried out on Horiba fluorolog TCSPC Spectrofluorimeter. 310 nm nano LED was used for excitation.

3. Results and discussions

The prepared samples were characterized by X-ray Diffraction for phase confirmation. The XRD pattern with all the indexed peaks is found to match with the JCPDS card no. 45-0550 as shown in Fig. 1, clearly indicating the formation of single phase rhombohedral unit cell. After Ce^{3+} doping, the pattern remains similar (Fig. 1b), indicating that there is no structural change due to doping.

The crystal structure properties such as lattice parameters and cell volume were obtained by Rietveld refinement of obtained XRD pattern of undoped $Ca_{10}Li(PO_4)_7$ using Fullprof suite software. Fig. 2 is a representative refined result, which displays the experimental and calculated XRD profile. It reveals that the phosphor crystallizes in Rhombohedral system with the space group R3c (No. 161) and refined cell parameters $a = b = 10.3846$ Å, $c = 37.3385$ Å, $Z = 6$, and $V = 3487.0916$ Å^3. These values are in good agreement with the literature [1,7]. The goodness of fit is $\chi^2 = 3.13$.

Fig. 3 shows SEM for $Ca_{10}Li(PO_4)_7$. Particles are in form of regular platelets of size 5–10 μm.

Fig. 4(A) shows reflectance spectra of the doped samples. In $Ca_{10}Li(PO_4)_7$:Ce^{3+} (curve a), onset of a strong absorption band is at about 375 nm. Minima are observed around 315, 295 and 265 nm. These correspond to absorption bands of Ce^{3+}. Host absorption is expected to prevail at the shorter wavelengths [7]. In the reflectance curve for $Ca_{10}Li(PO_4)_7$:Ce^{3+},Nd^{3+} (curve b) several additional sharp lines are observed in the region 430–630 nm. These correspond to f–f transitions of Nd^{3+}. Lines can be clearly distinguished at 517, 526 ($^4I_{9/2} \rightarrow {}^2K_{13/2}$, $^4G_{7/2}$) and 592 nm ($^4I_{9/2} \rightarrow {}^4G_{5/2}$, $^2H_{11/2}$). For getting better view, Kubelka-Munk function $F(R) = (1 - R)^2/2R$, where R is the reflectance, is plotted as a function of wavelength (Fig. 4B).

Fig. 5 shows PL emission spectra for $Ca_{10}Li(PO_4)_7$:Ce^{3+}. Intense emission is seen around 365 nm when the phosphors were excited by 320 nm. This is in good agreement with the value of 370 nm reported by Zhang et al. [7]. The intensity goes on increasing with Ce^{3+} concentration till 5 mol%. Concentration quenching is observed for higher concentrations (Fig. 5,

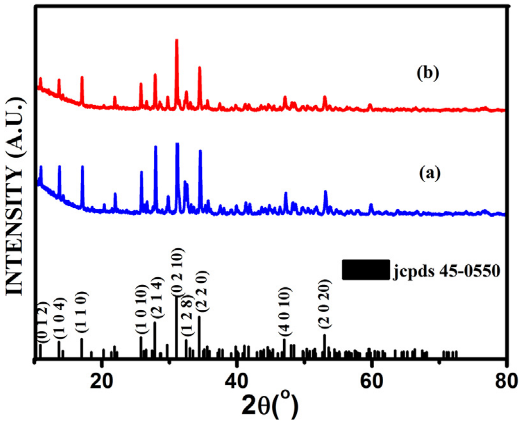

Fig. 1. XRD pattern of $Ca_{10}Li(PO_4)_7$ (a) and $Ca_{10}Li(PO_4)_7$:Ce^{3+} (b) compared with ICDD data.