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Light conversion material: $\text{LiBaPO}_4:\text{Eu}^{2+}$, Pr^{3+} , suitable for solar cell

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A light conversion material $\text{LiBaPO}_4:\text{Eu}^{2+}$, Pr^{3+} is successfully developed as a solar spectral converter for Si solar cells. The photoluminescence excitation and emission spectra from 3 K to room temperature, the lifetime and energy transfer mechanism are all systematically investigated. The results show that Eu^{2+} ions absorb and transfer the energy of UV-Vis photons to Pr^{3+} ions, which exhibit an intense near-infrared (NIR) emission between 950–1060 nm, matching well with the maximum spectral response of Si solar cells. We believe that this NIR emitting phosphor may open a new route to design advanced UV-Vis-to-NIR phosphors, with promising applications for solar spectral converters.

1. Introduction

Phosphors doped with rare earth ions (Re^{n+}) are used for many devices such as white light emitting diodes (WLED), displays and so on.^{1–3} Recently, they have also attracted much interest for photovoltaic applications to improve solar cell efficiency by modifying the solar spectrum. Si solar cells effectively convert near infrared (NIR) photons of lower energy close to the semiconductor band gap ($E_g \approx 1.12$ eV, $\lambda \approx 1000$ nm). However, the strongest emission of the solar spectrum is located in the UV-Vis region. The mismatch between the strongest emission in the solar spectrum and the spectral response of Si solar cells, will reduce the photoelectric conversion efficiency of the cell.^{4,5}

Recently, light conversion material is used to modify the solar spectrum and enhance the external quantum efficiency of Si solar cell.^{6–8} Many researches have been developed phosphors doped by Yb^{3+} ion, $\text{Eu}^{3+}-\text{Yb}^{3+}$, $\text{Tb}^{3+}-\text{Yb}^{3+}$, $\text{Dy}^{3+}-\text{Yb}^{3+}$, $\text{Eu}^{2+}-\text{Yb}^{3+}$ and so on.^{9–15} However, Yb^{3+} usually has no direct absorptions in UV-Vis (300–800 nm) range since it only has a single excited state $^2\text{F}_{5/2}$ approximately $10\,000\text{ cm}^{-1}$ above the ground state $^2\text{F}_{7/2}$. Therefore, Re^{3+} (Eu^{3+} , Tb^{3+} , Dy^{3+} and so on) is selected as a sensitizer in $\text{Re}^{3+}-\text{Yb}^{3+}$ co-doped phosphor. But this kind of materials usually have low absorption efficiency in UV-Vis light range, due to the forbidden 4f–4f transitions by the parity selection rule.

As we know, Pr^{3+} ion has the ability to absorb visible photons and emits NIR photons, because of its abundant energy levels in UV-Vis-NIR range. For instance, Pr^{3+} ion doped phosphors can be excited at the range of 440–700 nm due to the transitions from $^3\text{H}_4$ to $^1\text{D}_2$ (~ 600 nm), $^3\text{P}_j$ ($J = 0, 1, 2$) and $^1\text{I}_6$ (440–490 nm),

and emit NIR phonons at ~ 1000 nm ascribed to the $^3\text{P}_0 \rightarrow ^1\text{G}_4$ and/or $^1\text{G}_4 \rightarrow ^3\text{H}_4$, matching well with the optimal spectral response of Si solar cells.^{16–19} To enhance the absorption of Pr^{3+} in ultraviolet region, here we explored a promising light conversion phosphor $\text{LiBaPO}_4:\text{Eu}^{2+}$, Pr^{3+} for Solar Spectral Converter. It can exhibit an intense NIR emission of Pr^{3+} ion at about 1000 nm upon excitation with allowed 4f–5d absorption of Eu^{2+} ions.

2. Experiment

2.1 Syntheses

All phosphors were prepared by a conventional solid-state method. The stoichiometric amounts of LiH_2PO_4 (97%), BaCO_3 (A.R.), $\text{NH}_4\text{H}_2\text{PO}_4$ (A.R.), Eu_2O_3 (99.99%) and Pr_6O_{11} (99.99%) were used as raw materials. Then the ingredients were thoroughly grinded in an agate mortar and transferred into crucibles. Finally, the mixtures were sintered at 1200 °C for 3 h under N_2/H_2 (10 : 1) atmosphere and grounded homogeneously after cooling.

2.2 Measurements

The phase purity of the as-prepared phosphors was investigated by a Rigaku D/max-III A X-ray Diffractometer with Cu K α radiation ($\lambda = 1.5406$ Å) at 40 kV and 30 mA. The XRD patterns were collected in range of $15^\circ \leq 2\theta \leq 58^\circ$.

The photoluminescence (PL) and photoluminescence excitation (PLE) spectra from 3 K to room temperature as well as the decay curves were measured by FSP920 Time Resolved and Steady State Fluorescence Spectrometers (Edinburgh Instruments) equipped with a 450 WW Xe lamp, a 100 W μF920H lamp, TM300 excitation monochromator and double TM300 emission monochromators, red sensitive PMT and R5509-72 NIR-PMT in a liquid nitrogen cooled housing (Hamamatsu Photonics K.K.). The spectral resolution for the steady

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measurements is about 0.05 nm in UV-vis and about 0.075–0.01 nm in NIR, and the experimental conditions for the transient measurements are a pulse width of 1–2 μ s, a repetition rate of 50 Hz and the lifetime range of 100 μ s–200 s. For PL and PLE measurements at 3 K, the sample was mounted in a Optistat AC-V12 actively cooled optical cryostat, based on 0.25 W @ 4 K PTR (pulse tube refrigerator), with a ITC503 temperature controller and a water cooled compressor.

3. Results and discussion

3.1 Phase and structure characterization

The XRD patterns of polycrystalline samples $\text{LiBaPO}_4:\text{Eu}_x^{2+}, \text{Pr}_y^{3+}$ ($x = 0, y = 0; x = 0.005, y = 0, 0.005; x = 0, y = 0.01$) are shown in Fig. 1a. The results indicate that all the peaks of rare earth ions doped LiBaPO_4 can be indexed to the Joint Committee On Powder Diffraction Standard card of a pure LiBaPO_4 (JCPDS 14-0270), and also match well with the reference data.^{20,21} No detectable impurity phases were observed, which indicated that the introduction of dopants has no obvious influence on the crystalline structure of the host, which crystallize in a stuffed tridymite structure with a hexagonal unit cell and space group $P6_3$. Each PO_4 tetrahedron is jointed with four LiO_4 tetrahedron, while each LiO_4 is jointed with four PO_4 tetrahedrons, and two series of tetrahedron are linked by corner sharing,²¹ as shown in Fig. 1b and c. Furthermore, the ionic radius of Eu^{2+} , Pr^{3+} , Ba^{2+} and Li^+ are 1.25 Å, 1.13 Å, 1.42 Å and 0.92 Å, respectively. According to the ionic size and valence state of cationic, Eu^{2+} and Pr^{3+} ions are expected to replace the site of Ba^{2+} ion, since the radius of Eu^{2+} and Tb^{3+} are closed to that of Ba^{2+} .

3.2 Luminescence properties of $\text{LiBaPO}_4:\text{Pr}^{3+}$

Fig. 2 shows the PL (a and b) and PLE (c) spectra, and decay curves of $\text{LiBaPO}_4:\text{Pr}_{0.01}^{3+}$ at 3 K. The selection of low test

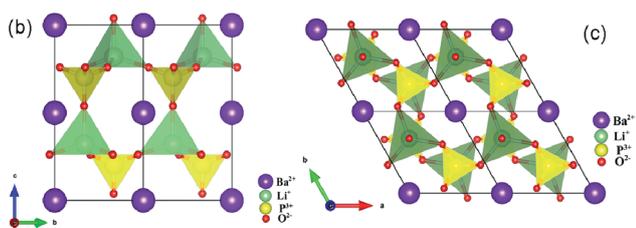
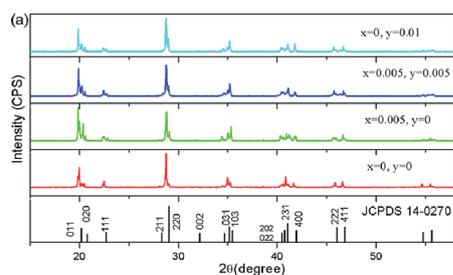


Fig. 1 XRD patterns of $\text{LiBaPO}_4:\text{Eu}_x^{2+}, \text{Pr}_y^{3+}$ ($x = 0, y = 0; x = 0.005, y = 0, 0.005; x = 0, y = 0.01$) (a), and schematic diagram of the structure of LiBaPO_4 along the a- (b) and c-direction (c).

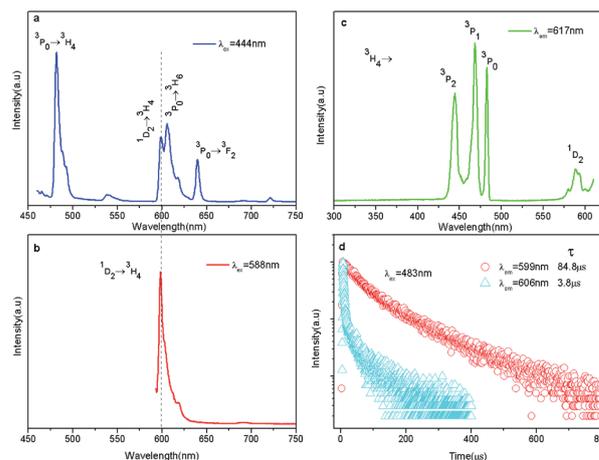


Fig. 2 PL (a and b) and PLE (c) spectrum, and decay curves (d) of $\text{LiBaPO}_4:\text{Pr}_{0.01}^{3+}$ at 3 K.

temperature is to reduce the effects of the host vibration or phonons on the optical properties of Pr^{3+} ion. As shown in Fig. 2c, the excitation spectrum mainly contains four sharp peaks at 444 nm, 468 nm, 483 nm and 588 nm, which are due to the absorption transitions of $^3\text{H}_4 \rightarrow ^3\text{P}_2, ^3\text{H}_4 \rightarrow ^3\text{P}_1$ and $^1\text{I}_6, ^3\text{H}_4 \rightarrow ^3\text{P}_0$, and $^3\text{H}_4 \rightarrow ^1\text{D}_2$ of Pr^{3+} ion, respectively, monitoring the emission at 617 nm. Fig. 2a and b are the emission spectra of Pr^{3+} ion under excitation from the ground state to the $^3\text{P}_2$ and $^1\text{D}_2$ levels, respectively. It is obviously that the emission spectrum excited to $^1\text{D}_2$ levels (Fig. 2a) consists of only one emission peak at 599 nm, due to the transitions from $^1\text{D}_2$ to $^3\text{H}_4$. Whereas excited to $^3\text{P}_2$ level (Fig. 2b), the emission spectrum consists of not only the emission from $^3\text{P}_0$ to $^3\text{H}_4, ^3\text{H}_6$ and $^3\text{F}_2$ peaked at 482 nm, 606 and 640 nm, but also the emission from $^1\text{D}_2$ to $^3\text{H}_4$ at 599 nm.

In order to clarify the assignment of the emissions peaks at 599 nm and 606 nm as shown in Fig. 2a, the luminescence decay curves at 3 K ($\lambda_{\text{ex}} = 483$ nm and 599 nm, $\lambda_{\text{em}} = 606$ nm) of $\text{LiBaPO}_4:\text{Pr}_{0.01}^{3+}$ were measured and presented in Fig. 2d. Generally, the decay time of the emission from $^1\text{D}_2$ is 50–250 μ s, longer than that from $^3\text{P}_0$, which is about 0.135–50 μ s.²² It is clear that the decay curves have different characteristics and the average lifetimes are calculated to be about 84.8 μ s and 3.8 μ s when excited to $^3\text{P}_0$ and $^1\text{D}_2$ level, respectively. Therefore, it is reasonable to assign the emission peaks at 599 nm and 606 nm to $^1\text{D}_2 \rightarrow ^3\text{H}_4$ and $^3\text{P}_0 \rightarrow ^3\text{H}_6$ transitions.

However, why can the emission from $^1\text{D}_2$ to $^3\text{H}_4$ be detected when excited into $^3\text{P}_2$ level? The energy transfer through multiphonon relaxation and cross-relaxation process may give a clear interpretation. Fig. 3 presents the schematic diagrams of Pr^{3+} in LiBaPO_4 . It is widely accepted that the electrons excited to $^3\text{P}_2$ level (2a) are able to relax to $^3\text{P}_0$ level assisted by phonons (process 2b), because of the small energy difference between $^3\text{P}_2$ and $^3\text{P}_0$ level. There are two possible non-radiative path to generate the $^1\text{D}_2 \rightarrow ^3\text{H}_4$ transition (process 2c and 2d). One is the non-radiative relaxation from $^3\text{P}_0$ to $^1\text{D}_2$ level assisted by phonons, which is labeled as process 2c. The energy difference between $^3\text{P}_0$ and $^1\text{D}_2$ level is about 3697 cm^{-1} . The maximum



a excited level to a ground level, it is expected to have the approximated lifetime when up to the same excited levels. The lifetimes of emission at 1020 nm are 0.125 ms and 0.136 ms excited to 3P_0 level (483 nm) and 1D_2 level (588 nm), respectively. Similarly, the lifetimes of emissions at 993 nm and 976 nm are 0.085 ms and 0.068 ms excited to 1D_2 level (588 nm). That is to say the emissions at 993 nm and 976 nm belong to the same transition, different to the 1020 nm. It is clearly that the lifetime of emission at 1020 nm is longer than that of the 993 nm and 976 nm because of the two steps of cross-relaxation processes. Therefore, the emissions at 976 nm (or 993 nm) and 1020 nm are attributed to the transitions of $^1D_2 \rightarrow ^3F_4$ and $^1G_4 \rightarrow ^3H_4$, respectively.

According to the report of A. Meijerink,²⁴ the absorption of a photon to the 3P_7 or 1I_6 levels would be followed by the emission of two NIR photons, whereas absorption to 1D_2 would result in emission of only one NIR photon. If the area ratio (R_E) of the 3P_7 and 1I_6 band to 1D_2 band in the excitation spectrum is twice as large as the ratio (R_A) similarly obtained in the absorption spectra, the quantum cutting will be efficient. Fig. 5c and d show the excitation spectrum and the absorption spectrum of $\text{LiBaPO}_4:\text{Pr}_{0.01}^{3+}$. It can be found in Fig. 5c and d that the R_E and R_A are 4.0 and 4.4, respectively. It means that the blue-to-NIR quantum cutting process from the 3P_0 level does not occur in LiBaPO_4 .

As mentioned above, the ideal light conversion material for Si solar cells should utilize the UV-vis region of the solar spectrum and possess an intense NIR emission, matching well with the maximum spectral response ($\lambda \approx 1000$ nm) of Si semiconductor. As shown in Fig. 5a and c, $\text{LiBaPO}_4:\text{Pr}^{3+}$ meets the requirement of excitation and emission characteristics of light conversion material. However, it can only absorb the photons in blue and red region of the solar spectrum. Unfortunately, the intensity of the excitation peaks is very weak because the 4f–4f absorption transitions are forbidden by the parity selection rule. In order to widen the utilization of the solar spectrum towards UV region, we further investigate the luminescent properties of $\text{LiBaPO}_4:\text{Eu}^{2+}, \text{Pr}^{3+}$ and explore the possibility of Eu^{2+} ion as donor absorbing UV photons, which greatly enhances the NIR emission of Pr^{3+} ion through efficient energy feeding by allowed 4f–5d absorption of Eu^{2+} ion with high oscillator strength.

3.3 Luminescence properties of $\text{LiBaPO}_4:\text{Eu}_{0.005}^{2+}, \text{Pr}_{0.005}^{3+}$

As discussed above, $\text{LiBaPO}_4:\text{Eu}_{0.005}^{2+}, \text{Pr}_{0.005}^{3+}$ phosphor shows the optimal NIR performance. In order to explore its possibility of potential application in Si solar cells, as shown in Fig. 6c. It is obviously seen that Si solar cells most effectively convert photons of energy close to the semiconductor band gap ($E_g \approx 1.12$ eV, 1000 cm^{-1}), but the incident solar spectrum dominates in UV-Vis region. This mismatch between the incident solar spectrum and the spectral response of Si solar cells is one of the main reasons to limit the efficiency of cell. For instance, a UV photon with high energy (250–425 nm) directly creates an electron–hole (e–h) pair in Si solar cells (Fig. 3a). However, the photo-excited pair quickly loses energy in excess of band gap of Si and the extra energy is lost as heat within the device (Fig. 3b).

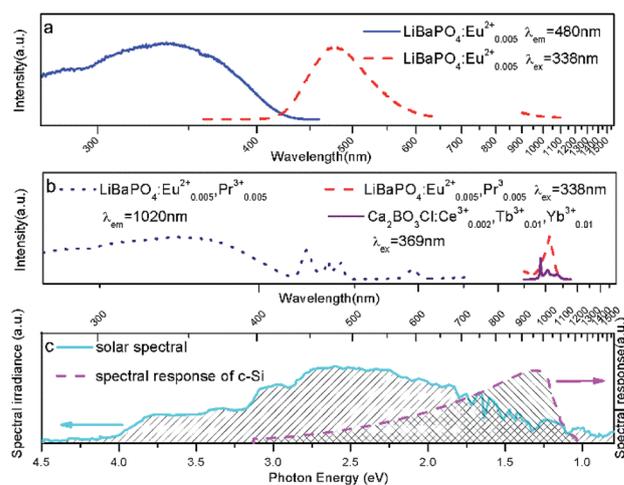


Fig. 6 PLE and PL spectra of $\text{LiBaPO}_4:\text{Eu}_{0.005}^{2+}$ (a), $\text{LiBaPO}_4:\text{Eu}_{0.005}^{2+}, \text{Pr}_{0.005}^{3+}$, $\text{Ca}_2\text{BO}_3\text{Cl}:\text{Ce}_{0.002}^{3+}, \text{Tb}_{0.01}^{3+}, \text{Yb}_{0.01}^{3+}$ (b) at room temperature and the solar spectral and spectral response of c-Si (c).

Consequently, the heat energy leads to the thermalization of the charge carriers. In summary, the efficiency of Si solar cells is limited because of the energy loss resulting from thermalization of the charge carriers generated by the absorption of high-energy photons. But if UV-vis photons can be converted into NIR photons prior to absorption into Si solar cells (as shown in Fig. 3c), the charges thermalization of Si solar cells will be greatly decreased and the efficiency of Si solar cells will be improved.

Fig. 6a exhibits the PLE and PL spectra of $\text{LiBaPO}_4:\text{Eu}_{0.005}^{2+}$, which contains 4f–5d allowed transition of Eu^{2+} ions at 250–425 nm and a blue emission band at 480 nm.²¹ It is worth noting that the Eu^{2+} single doped LiBaPO_4 has no emission band at NIR range. Fig. 6b gives the PLE and PL spectra of $\text{LiBaPO}_4:\text{Eu}_{0.005}^{2+}, \text{Pr}_{0.005}^{3+}$. Monitoring the emission at 1020 nm, the PLE spectrum contains a broad band and some sharp peaks. Comparing the PLE spectra of Eu^{2+} or Pr^{3+} singly doped in LiBaPO_4 phosphors (Fig. 6a and 2c), the intense broad band centered at 338 nm should be attributed to 4f–5d allowed transition of Eu^{2+} ions. The other peaks at 444 nm, 468 nm, 483 nm and 590 nm are due to f–f transitions of Pr^{3+} ions. Similar as Fig. 5a, the emission band peaked at 1020 nm is attributed to transition of $^1G_4 \rightarrow ^3H_4$ of Pr^{3+} . The appearance of 4f \rightarrow 5d transitions of Eu^{2+} ions in the PLE spectrum and the existence of the $^1G_2 \rightarrow ^3H_4$ transitions of Pr^{3+} ion in the PL spectrum of $\text{LiBaPO}_4:\text{Eu}_{0.005}^{2+}, \text{Pr}_{0.005}^{3+}$ indicate that the energy transfer from Eu^{2+} to Pr^{3+} occurs, as shown in Fig. 3. It demonstrates that $\text{LiBaPO}_4:\text{Eu}^{2+}, \text{Pr}^{3+}$ can harvest UV-Vis photons of the incident solar spectral and significantly reduce the charges thermalization of Si solar cells by UV/vis-to-NIR spectral modification. At the same time, we compared our material with $\text{Ca}_2\text{BO}_3\text{Cl}:\text{Ce}_{0.002}^{3+}, \text{Tb}_{0.01}^{3+}, \text{Yb}_{0.01}^{3+}$, which was promising as useful light convert material for solar cell.²⁵ It is obviously that the emission intensity of our phosphor is about 5 times as intense as $\text{Ca}_2\text{BO}_3\text{Cl}:\text{Ce}_{0.002}^{3+}, \text{Tb}_{0.01}^{3+}, \text{Yb}_{0.01}^{3+}$ in NIR area. Therefore, it can be a promising light conversion material to increase the efficiency of Si solar cells.



4. Conclusions

Light conversion material $\text{LiBaPO}_4:\text{Eu}^{2+}, \text{Pr}^{3+}$ was systematically investigated. We studied the spectral assignment of Pr^{3+} ions, and proved that the emissions at 599 nm and 617 nm are attributed to the $^1\text{D}_2 \rightarrow ^3\text{H}_4$ and $^3\text{P}_0 \rightarrow ^3\text{H}_6$ transfer according to the study of luminescence decay and spectra at low temperature. It is demonstrated that the energy transfer from Eu^{2+} to Pr^{3+} occurs in this matrix. Therefore, this phosphor has a wide excitation band in UV-vis region and emits intense NIR emitting around 1000 nm, which is matching well with the maximum spectral of Si solar cells. From the viewpoint of spectral modification, it may be a new light conversion material to match the solar spectrum and the spectral response of Si solar cells.

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