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COMMUNICATION

An intense NIR emission from $\text{Ca}_{14}\text{Al}_{10}\text{Zn}_6\text{O}_{35}:\text{Mn}^{4+},\text{Yb}^{3+}$ via energy transfer for solar spectral convertor

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To date, most current reports on the development and optimization of solar spectral converter have utilized the energy transfer among the rare-earth ions. Here we introduce a non-rare-earth ion Mn^{4+} to transfer the energy to Yb^{3+} , which can exhibit strong near-infrared luminescence. It can harvest UV-Blue photons and exhibits an intense NIR emission of Yb^{3+} around 1000 nm, perfectly matching the maximum spectral response of Si solar cells. It demonstrates for the first time that efficient energy transfer is occurred by a decrease in the excited state lifetime and red photoluminescence (PL) from Mn^{4+} with increasing Yb^{3+} concentration. These results demonstrate that the Mn^{4+} ions can be an efficient and direct sensitizer harvesting UV-blue photons. It could provide new avenues for developing harvesting Si-based solar cells.

Rare-earth ions, as widely used activators, have been playing an irreplaceable role in modern lighting and bioimaging fields due to their abundant emission colors based on the 4f-4f or 5d-4f transitions.¹⁻⁴ Especially, the Yb^{3+} ion, which is located close to the maximum of the spectral efficiency of c-Si solar cells, has been identified as an almost ideal acceptor species for this purpose.⁵⁻⁹ However, unlike the metal ions, Yb^{3+} ion usually has no direct absorptions in the UV-Vis (300–800 nm) range.^{10,11} Consequently, it is necessary to add codopants primarily rare-earth ions, for instance RE^{3+} (RE = Ce, Eu, Tb, Pr) ions acting as the sensitizer, to absorb UV-Vis photons and transfer the energy to Yb^{3+} ion, or the metal ions, such as Bi^{3+} and Cr^{3+} , are chosen as the energy donors for Yb^{3+} to realize the broadband spectral conversion.¹²⁻²¹

Mn^{4+} -activated compounds, usually as a class of non-rare-earth phosphors with high-efficacy and attractive luminescence properties, has showed great promise of as commercial red luminescent material in warm white LEDs.²²⁻²⁶ Recently, we developed a highly efficient Mn^{4+} activated $\text{Ca}_{14}\text{Al}_{10}\text{Zn}_6\text{O}_{35}$ phosphor,

they exhibit the most intense broadband excitation at 460 nm with a bandwidth of 50 nm and very sharp emission lines peaking at 700nm as a result of stronger crystal field for Mn^{4+} .²⁷ These unique optical characteristics meet the spectral requirements for an ideal solar spectral converter, and thus we codoped the Yb^{3+} and expected near-infrared emitting as promising of Si solar cells. So far, most of previous efforts were devoted to the optical properties investigation of energy transfer among the rare-earth ions. To the best of our knowledge, c-Si solar cells based on the energy transfer from non-rare-earth Mn^{4+} , a new approach to obtaining NIR emission, had never been achieved before.

In this work, we introduce a non-rare-earth ion Mn^{4+} to transfer the energy to Yb^{3+} , an intense near-infrared emitting is successful realized. Particularly, it is thus reasonable to infer that the Mn^{4+} ion may be a promising sensitizer for Yb^{3+} ion, which would provide a novel route for the development of c-Si solar cells.

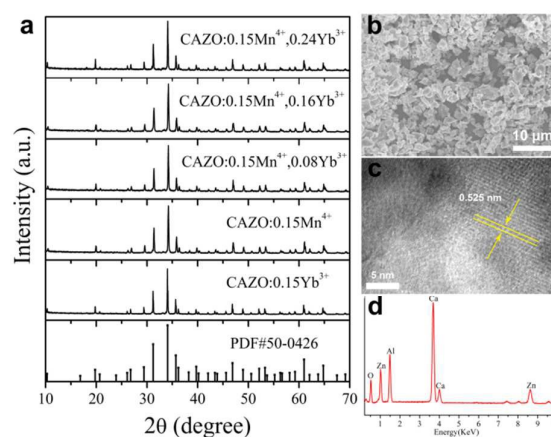


Figure 1. XRD (a), SEM (b), High-resolution TEM image (c) and EDS pattern (d) of the CAZO: $\text{Mn}^{4+},\text{Yb}^{3+}$ powders.

The measurements on the powder x-ray diffraction for the samples were performed to verify the phase purity. The XRD patterns of all samples are the same to each other, as presented in Fig. 1a, indicate that the substitution of doping ions do not

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significantly influence the crystal structure. Fig. 1b presents the typical SEM images of samples. The morphology of the sample synthesized at 1220°C exhibits irregular spheroidicity with particle sizes below 5 μm . High-resolution transmission electron microscopy (HRTEM) images of $\text{Ca}_{14}\text{Al}_{10}\text{Zn}_6\text{O}_{35}$, shown in Fig. 1c, confirmed the ordered structure. These results show that well-crystallized $\text{Ca}_{14}\text{Al}_{10}\text{Zn}_6\text{O}_{35}:\text{Mn}^{4+}$ powders have been obtained. The corresponding EDX spectrum analysis (Fig. 1(d)) indicates that the product has a chemical composition of Ca, Al, Zn and O, and that no impurity elements are present.

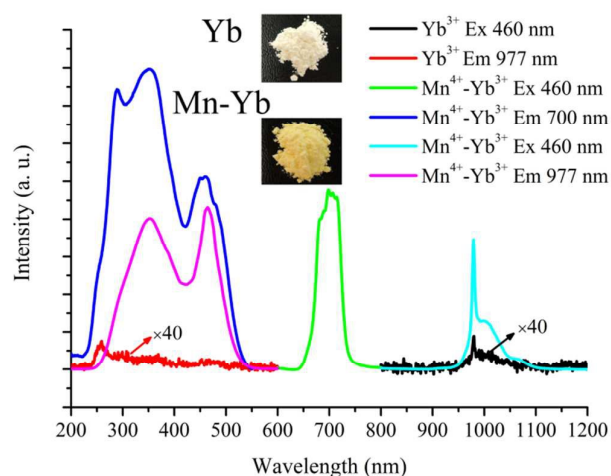


Figure 2. PL and PLE spectra and corresponding body colors (inset) of the CAZO: Yb^{3+} and CAZO: $\text{Mn}^{4+}, \text{Yb}^{3+}$ samples.

Yb^{3+} doping of $\text{Ca}_{14}\text{Al}_{10}\text{Zn}_6\text{O}_{35}$ yielded white body color, while the $\text{Ca}_{14}\text{Al}_{10}\text{Zn}_6\text{O}_{35}:\text{Mn}^{4+}, \text{Yb}^{3+}$ revealed yellow body color, as shown in Figure 2 inset. Under near-UV to blue irradiation, $\text{Ca}_{14}\text{Al}_{10}\text{Zn}_6\text{O}_{35}:\text{Yb}^{3+}$ shows no luminescence; in contrast, after introduce non-rare-earth ion Mn^{4+} into $\text{Ca}_{14}\text{Al}_{10}\text{Zn}_6\text{O}_{35}:\text{Yb}^{3+}$, the sample exhibits strong luminescence in the NIR spectral region. Figure 2 shows the emission spectrum of the $\text{Ca}_{14}\text{Al}_{10}\text{Zn}_6\text{O}_{35}:\text{Yb}^{3+}$ and $\text{Ca}_{14}\text{Al}_{10}\text{Zn}_6\text{O}_{35}:\text{Mn}^{4+}, \text{Yb}^{3+}$ phosphor, as well as the corresponding excitation spectrum. According to our preliminary experiments, Mn^{4+} single doped $\text{Ca}_{14}\text{Al}_{10}\text{Zn}_6\text{O}_{35}$ give an efficient deep red-emitting. Figure S1 presented the absolute quantum yields of the $\text{Ca}_{14}\text{Al}_{10}\text{Zn}_6\text{O}_{35}:\text{Mn}^{4+}$ excited with different wavelength. The synthesized red phosphor shows an extremely high PL QY up to 90% under 300 nm excitation and also to 50% under 460 nm excitation. Here, the deep red emission centered at 700 nm is assigned to the ${}^2\text{E} \rightarrow {}^4\text{A}_2$ transition of Mn^{4+} ions, and the intense NIR emission centered at 978 nm is attributed to the lowest stark level of Yb^{3+} , ${}^2\text{F}_{2/5}$, to the stark level of the ground state of Yb^{3+} , ${}^2\text{F}_{7/2}$, respectively. By comparing the PL intensity of $\text{Ca}_{14}\text{Al}_{10}\text{Zn}_6\text{O}_{35}:\text{Mn}^{4+}, \text{Yb}^{3+}$ with $\text{Ca}_{14}\text{Al}_{10}\text{Zn}_6\text{O}_{35}:\text{Yb}^{3+}$, it can be seen that the PL spectrum of $\text{Ca}_{14}\text{Al}_{10}\text{Zn}_6\text{O}_{35}:\text{Yb}^{3+}$ is too weak to detect. Therefore, the effective resonance-type energy transfer from Mn^{4+} to Yb^{3+} is strongly expected. Moreover, the PLE spectra of $\text{Ca}_{14}\text{Al}_{10}\text{Zn}_6\text{O}_{35}:\text{Mn}^{4+}, \text{Yb}^{3+}$ monitored at 700 and 973 nm are similar except for the difference in intensity. It also means that the efficient ET from Mn^{4+} to Yb^{3+} occurs. Figure 3 displayed a partial structural overview of $\text{Ca}_{14}\text{Al}_{10}\text{Zn}_6\text{O}_{35}$ and the occupation of doping ions. The

Al^{3+} ion is coordinated with six O^{2-} ions to form a regular octahedron, as is reported, Mn^{4+} usually doped into AlO_6 polyhedra in view of similar ionic radius ($R[\text{Al}^{3+}] = 0.535 \text{ nm}$; $R[\text{Mn}^{4+}] = 0.53 \text{ nm}$). While Yb^{3+} can only substitute for the Ca^{2+} site in the $\text{Ca}_{14}\text{Al}_{10}\text{Zn}_6\text{O}_{35}$ lattices. Thus, we infer that the red emission is assigned to Mn^{4+} occupying Al^{3+} , and the other NIR emission corresponds to Yb^{3+} occupying Ca^{2+} . As shown in Fig. 3, a scheme mapping the possible energy processes occurring in the $\text{Ca}_{14}\text{Al}_{10}\text{Zn}_6\text{O}_{35}:\text{Mn}^{4+}, \text{Yb}^{3+}$ materials is also presented. The energy difference between the lowest ${}^2\text{E}$ excitation level (142857 cm^{-1}) of Mn^{4+} ion and the ${}^4\text{F}_{5/2}$ level (102249 cm^{-1}) of Yb^{3+} ion is about 40608 cm^{-1} . When Mn^{4+} ion absorbs one photon at 460 nm, the electron will decay nonradiatively to the ${}^2\text{E}$ state of Mn^{4+} . As we known, the energy of ${}^2\text{E}$ state is less than twice the energy of a Yb^{3+} : 978 nm photon, hence it can convert into only one Yb^{3+} : 978 nm photon, which means the ET from Mn^{4+} to Yb^{3+} is a single-photon process.

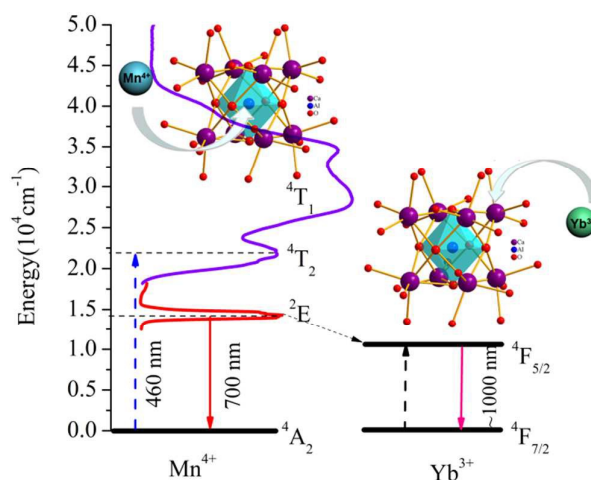


Figure 3. Schematic energy-level diagram of ET process and the occupation of doping ions in $\text{Ca}_{14}\text{Al}_{10}\text{Zn}_6\text{O}_{35}:\text{Mn}^{4+}, \text{Yb}^{3+}$ samples.

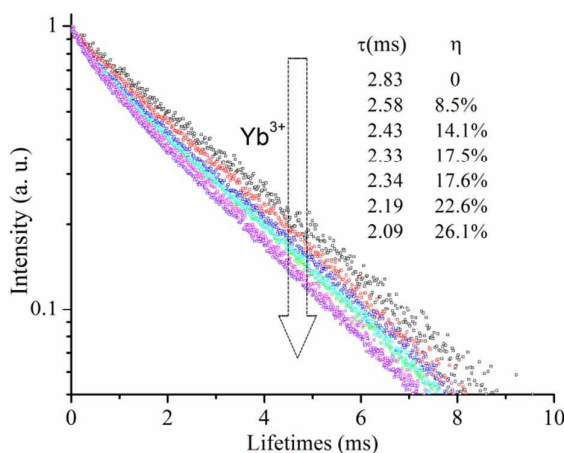


Figure 4. The fluorescence lifetimes of the Mn^{4+} ions monitored at 700 nm excited by 355 nm pulsed laser.

To analyze the mechanism of energy transfer, we thus synthesized the Mn^{4+} and Yb^{3+} codoped $\text{Ca}_{14}\text{Al}_{10}\text{Zn}_6\text{O}_{35}$ samples and

studied the corresponding luminescent behavior. Figure S2 depicts the emission spectra for the $\text{Ca}_{14}\text{Al}_{10}\text{Zn}_6\text{O}_{35}:\text{Mn}^{4+},\text{Yb}^{3+}$ with various concentrations of Yb^{3+} . The emission intensity of Yb^{3+} ions increases followed by emission decreases of Mn^{4+} due to $\text{Mn}^{4+}-\text{Yb}^{3+}$ energy transfer. Meanwhile, the effect of introducing Mn^{4+} and Yb^{3+} on the sensitizer ion decay curves of the series powders is indicated in Fig. 4. Compared with the decay curve of single doped ions in host, noticeable reduction of Mn^{4+} ions decay curves can be seen. The values of the lifetimes are obtained by integrating the decay curves, of which the initial intensities are normalized. The energy transfer efficiency η can be calculated using $\eta=1-\tau/\tau_0$, where τ and τ_0 are fluorescence lifetimes of Mn^{4+} with and without codoping of Yb^{3+} , respectively. The calculated energy transfer efficiency is shown in Fig. 4 inset. With increasing Yb^{3+} concentration, η increases and reaches 30 % at $y = 0.24$.

Conclusions

We have successfully developed a new approach to obtaining NIR emission from on-rare-earth Mn^{4+} for Si solar cells. It downconverts the UV-to-blue (300-500 nm) part of the solar spectrum to ~ 1000 nm photons, perfectly matching the maximum spectral response of Si solar cells. We demonstrate for the first time that Mn^{4+} ion can be an efficient sensitizer harvesting UV photons and greatly enhancing the NIR emission of Yb^{3+} ion through efficient energy transfer. We believe this new NIR phosphor may open a new route to the design of advanced NIR phosphors promising for Si solar cells.

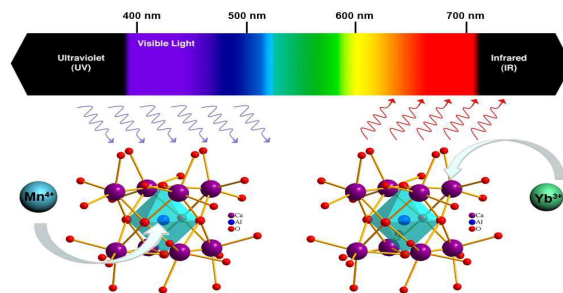
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Graphical abstract



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