Luminescence Properties and Energy Transfer in SrLa$_2$Sc$_2$O$_7$ Co-Doped with Bi$^{3+}$/M (M = Eu$^{3+}$, Mn$^{4+}$, or Yb$^{3+}$)

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Abstract: Series of Eu$^{3+}$/Mn$^{4+}$/Yb$^{3+}$-doped SrLa$_2$Sc$_2$O$_7$:Bi$^{3+}$ (SLSO: Bi$^{3+}$) were synthesized by a high-temperature solid-state method, and the energy transfer of Bi$^{3+}$→Eu$^{3+}$/Mn$^{4+}$/Yb$^{3+}$ was observed. Under ultraviolet radiation, a 550 nm emission peak was observed, which is attributed to Bi$^{3+}$ occupying the Sr$^{2+}$/La$^{3+}$ sites. Additionally, the other peaks were found to be 615, 707, and 980 nm, which are assigned to the Re$^{3+}$ (Eu$^{3+}$ and Yb$^{3+}$) and Mn$^{4+}$ occupying two different cationic sites. An obvious energy transfer (ET) from Bi$^{3+}$ to Eu$^{3+}$/Mn$^{4+}$/Yb$^{3+}$ was observed, and the tunable color, emitting from yellow to red, was obtained; the ET efficiency was about 86.2%, 78.6%, and 27.5% in SLSO, respectively. We found that the large overlap area between the emission spectrum of the sensitizer and the excitation spectrum of the activator could produce efficient energy transfer, which provided the idea for designing experiments in the future for some highly efficient energy transfer processes.

Keywords: luminescence; phosphor; energy transfer

1. Introduction

Recently, luminescent materials have been widely used in light-emitting diodes (LEDs), medical devices, 3D displays, temperature sensing, and other applications [1,2]. Being an essential component of LED devices, the different color emitting phosphors have been investigated and discussed; they are considered one of the biggest challenges in the field of lighting and backlighting display [3,4]. Generally, the different emitting phosphors can be achieved by energy transfer (ET) [5–12]. As is well known, Eu$^{3+}$, Ce$^{3+}$, and Bi$^{3+}$ are effective sensitizers because they can emit broad bands in various hosts, depending on their 4f$^0$5d$^1$−4f$^7$, 5d$^1$−4f$^6$, and 3P$_1$−S$_0$ allowed transitions [13–15], respectively, and can transfer the energy to activators, such as rare earth ions (Re$^{3+}$ = Eu$^{3+}$, Sm$^{3+}$, Tb$^{3+}$, Yb$^{3+}$, Nd$^{3+}$, etc.), and achieve the different color emitting phosphors [16–18]. The 6s$^2$ configuration of the Bi$^{3+}$ ion is sensitive to its surroundings of the local crystal field but is more stable than other valence states such as Bi$^{6+}$, Bi$^{2+}$, and Bi$^{5+}$; hence, Bi$^{3+}$ ion exhibits a variety of emissions involving ultraviolet, blue, green, yellow, and red [19–21]. In contrast, unique spectral features such as narrow emission bands, long luminescence lifetimes, and diverse emission states are presented by Re$^{3+}$ ions with a 4f electronic configuration [22]. Therefore, both are considered candidates for the potential of multiple luminescent color materials. In this work, in order to improve the luminescent properties of activator Eu$^{3+}$/Mn$^{4+}$/Yb$^{3+}$, we select SrLa$_2$Sc$_2$O$_7$ as the host and Bi$^{3+}$ as the sensitizer for multi-colored phosphors. In scandium salts, the Sc$^{3+}$ ion does not follow the contraction law of the lanthanides and possesses a smaller ionic radius. Due to the lack of 4f electrons, it has a different electron configuration than other rare earth elements, giving it special physicochemical properties that allow Sc-based matrices to exhibit excellent photoluminescence. We, therefore, chose SrLa$_2$Sc$_2$O$_7$ matrix crystals. In this paper, we choose the co-doping of Bi$^{3+}$→Eu$^{3+}$; Bi$^{3+}$→Mn$^{4+}$; Bi$^{3+}$→Yb$^{3+}$
to achieve visible to near-infrared light emission in the SrLa$_2$Sc$_2$O$_7$ matrix, with Bi$^{3+}$ as the sensitizer and Eu$^{3+}$/Mn$^{4+}$/Yb$^{3+}$ as the activator. It is noted that SrLa$_2$Sc$_2$O$_7$ had three cationic environments: SrO$_{12}$, Sr/LaO$_9$, and ScO$_6$ polyhedrals, respectively. The emission color can turn from yellow to red and near-infrared light by the Eu$^{3+}$, Yb$^{3+}$, and Bi$^{3+}$ entering into the Sr/LaO$_9$ polyhedral in terms of ion valence and radius and because the Mn$^{4+}$ ion has a small radius, which can occupy the ScO$_6$ site to produce the yellow to deep red light. Moreover, the luminescence properties and the energy transfer progress of Eu$^{3+}$/Mn$^{4+}$/Yb$^{3+}$/Bi$^{3+}$ in SrLa$_2$Sc$_2$O$_7$ are also discussed. We also explore the interaction between the sensitizer and the activator and find that the large overlap area between the emission spectrum of the sensitizer and the excitation spectrum of the activator produces efficient energy transfer, which provides the idea for designing experiments in the future for some highly efficient energy transfer processes.

2. Materials and Methods

A series of SrLa$_2$Sc$_2$O$_7$:0.06Bi$^{3+}$, Re$^{3+}$ (Re = Eu and Yb) and SrLa$_2$Sc$_2$O$_7$:0.06Bi$^{3+}$, Mn$^{4+}$ was synthesized by the high-temperature solid-state method. High purity SrCO$_3$ (99.99%), La$_2$O$_3$ (99.99%), Sc$_2$O$_3$ (99.99%), Bi$_2$O$_3$ (99.99%), Eu$_2$O$_3$ (99.99%), MnO$_2$ (99.99%), and Yb$_2$O$_3$ (99.99%) were used as raw materials. The ingredients are mixed together thoroughly in an agate mortar for 10 min according to the stoichiometric proportions. The raw materials were then placed in a crucible and heated at 900 °C for 6 h, and then at 1500 °C for 6 h. Finally, by cooling the synthetic samples to room temperature, it was then ground into a powder for subsequent measurement.

Samples were analyzed by a Bruker D8 X-ray diffractometer (XRD) under Cu Kα radiation at 40 kV and 40 mA, with the radiation source parameters set to $\lambda = 1.5406$ Å, $\theta = 10–80^\circ$, and step sizes = 0.05 s/step. Rietveld structure were carried out using the General Structural Analysis System (GSAS) software (version 1251). The excitation and emission spectra were measured by a Japan Hitachi F-7000 fluorescence spectrometer; its resolution can reach 1 nm. The decay curves were recorded on a HORIBA FLuoLog-3 fluorescence spectrometer; the instrument can measure lifetime values from 10 ps to 10 s.

3. Results and Discussion

3.1. Phase Information

Generally, the performance of phosphor is affected by the crystal structure [23]. Figure 1a depicts the crystal structure of the SrLa$_2$Sc$_2$O$_7$ unit cell and the crystal structure of the SrLa$_2$Sc$_2$O$_7$ orthorhombic system and the Pmmn space group. It is revealed that the Sr1, Sr2/La, and Sc sites are surrounded by oxygen atoms with the coordination numbers of 12, 9, and 6, respectively. It is worth noting that the [Sr1O$_{12}$], [Sr2O$_8$] polyhedral and the [ScO$_6$] octahedra are joined together by shared edges to form the basic unit. Figure 1b–d present the standard XRD pattern of SrLa$_2$Sc$_2$O$_7$ (SLSO) (ICSD#67625), the XRD patterns of SLSO:0.06Bi$^{3+}$, yEu$^{3+}$ (y = 0, 0.0125, 0.025, 0.05, 0.1, and 0.15), SLSO:0.06Bi$^{3+}$, mMn$^{4+}$ (m = 0, 0.001, 0.003, 0.005, 0.007, 0.01, and 0.015), and SLSO:0.06Bi$^{3+}$, zYb$^{3+}$ (z = 0.01, 0.015, 0.02, 0.05, and 0.15). The Rietveld refinement of the XRD patterns obtained by slow sweeping using the GSAS program is required. Here, a series of SLSO: Bi$^{3+}$, Eu$^{3+}$/Mn$^{4+}$/Yb$^{3+}$/Bi$^{3+}$, and SLSO: Bi$^{3+}$, Yb$^{3+}$ was refined separately, and the diffraction peaks of all samples were basically consistent with the standard card (ICSD#67625). Figure 1e–g show the Rietveld refinement results for the representative samples of the Eu$^{3+}$/Mn$^{4+}$/Yb$^{3+}$/Bi$^{3+}$-doped SLSO: Bi$^{3+}$. The black "−" indicates the intensity obtained from experimental tests, the blue dot represents the calculated intensity, the green line indicates the background, the green horizontal line indicates the error between the intensity obtained from experimental tests and the calculated intensity, and the plum-red "↑" indicates the Bragg reflection position of the calculated pattern. The refinement parameters $R_{wp} < 15\%$, $R_p < 10\%$, and $\chi^2 < 5$ are within a reasonable range. These indicate that the Eu$^{3+}$/Mn$^{4+}$/Yb$^{3+}$/Bi$^{3+}$ incorporation into the SLSO could maintain the phase purity and no impurity phase was generated at the current doping level.
SLSO could maintain the phase purity and no impurity phase was observed from the emission spectra of SLSO:0.06Bi$^{3+}$; while these sharp peaks are associated with the 4f-4f characteristic transitions of Eu$^{3+}$ ions. Under the 350 nm excitation, as shown in Figure 2b, not only a broad emission band centered at 550 nm but also several sharp peaks at 581, 590, 598, 615, 658 nm excitation, which can be attributed to the $^7F_0 \rightarrow ^3P_1$ transition of Bi$^{3+}$ ions and a charge transfer band (CTB) transition (Eu$^{3+}$-$\text{O}^2$), while these sharp peaks are associated with the 4f-4f characteristic transitions of Eu$^{3+}$ ions. Under the 350 nm excitation, as shown in Figure 2b, not only a broad emission band centered at 550 nm but also several sharp peaks at 581, 590, 598, 615, 658, and 707 nm were observed from the emission spectra of SLSO:0.06Bi$^{3+}$, yEu$^{3+}$, SLSO:0.06Bi$^{3+}$, mMn$^{4+}$, and SLSO:0.06Bi$^{3+}$, zYb$^{3+}$; (e-g) Refined results of SLSO:0.06Bi$^{3+}$, 0.05Eu$^{3+}$, SLSO:0.06Bi$^{3+}$, 0.007Mn$^{4+}$, and SLSO:0.06Bi$^{3+}$, 0.02Yb$^{3+}$.

3.2. Luminescence Properties of SLSO:0.06Bi$^{3+}$, yEu$^{3+}$

Figure 2a shows the emission and excitation spectra of SLSO:0.06Bi$^{3+}$, 0.05Eu$^{3+}$. For the 615 nm emission peak, the band centered at 350 nm, along with the characteristic absorption bands of Eu$^{3+}$ ions at 394, 465, and 537 nm, which can be attributed to the $^7F_0 \rightarrow ^5L_6$, $^7F_0 \rightarrow ^5D_2$, and $^7F_0 \rightarrow ^5D_1$ of Eu$^{3+}$ [24]. Moreover, the wide band is comprised of a $^1S_0 \rightarrow ^3P_1$ transition of Bi$^{3+}$ ions and a charge transfer band (CTB) transition (Eu$^{3+}$-$\text{O}^2$), while these sharp peaks are associated with the 4f-4f characteristic transitions of Eu$^{3+}$ ions. Under the 350 nm excitation, as shown in Figure 2b, not only a broad emission band centered at 550 nm but also several sharp peaks at 581, 590, 598, 615, 658, and 707 nm were observed from the emission spectra of SLSO:0.06Bi$^{3+}$, yEu$^{3+}$, which correspond to the $^5D_0 \rightarrow ^7F_j$ (j = 0, 1, 2, 3, 4) characteristic transitions of Eu$^{3+}$ ions. Among them, the 590 and 598 nm emission peaks, corresponding to the $^5D_0 \rightarrow ^7F_1$ transition, are magnetic dipole transitions and are insensitive to positional symmetry in the crystal structure, while the red emission at 615 nm is attributed to the $^5D_0 \rightarrow ^7F_2$ electric dipole transition [25–27], which arises from the lack of inversion symmetry at the Eu$^{3+}$ site; its emission intensity is much stronger than that of the transition $^7F_1$ level. When Eu$^{3+}$ ions are in a low-local symmetric environment, the $^5D_0 \rightarrow ^7F_2$ is dominant [28]. Considering the similar ionic radius and the same charge, Eu$^{3+}$ ions tend to occupy the position of La$^{3+}$ in SLSO. As can be observed in the spectrum, the $^5D_0 \rightarrow ^7F_2$ emission of Eu$^{3+}$ at 615 nm is the strongest emission peak.
Figure 2c, with the increase in Eu\(^{3+}\) concentration from \(y = 0\) to \(y = 0.15\), the red emission intensity at 615 nm appears to increase significantly, while the yellow emission intensity at 550 nm is constantly decreased, which shows the energy transfer from Bi\(^{3+}\) to Eu\(^{3+}\). The critical distance \(R_c\) is of great significance for evaluating the energy transfer mechanism from Bi\(^{3+}\) to Eu\(^{3+}\) in SLSO: Bi\(^{3+}\), Eu\(^{3+}\). The following equation can be used (see [29,30]):

\[
R_c \approx 2 \frac{3V}{4\pi x_c N} \left( \frac{1}{2} \right)
\]

where the \(x_c\) value is the critical concentration of dopant ions (total concentration of Bi\(^{3+}\) and Eu\(^{3+}\)), referring to the luminescence intensity of Bi\(^{3+}\) in SLSO: Bi\(^{3+}\), Eu\(^{3+}\), which is half of the initial value luminescence intensity; \(V\) is the cell volume size of 682.987 Å\(^3\); \(N = 4\). Therefore, the calculated \(R_c\) is 12.68 Å, excluding the exchange interaction mechanism \(R_c \approx 5\) Å. Thus, for SLSO: Bi\(^{3+}\), Eu\(^{3+}\), the electric multipole interaction is used for the energy transfer of Bi\(^{3+}\)-Eu\(^{3+}\). The energy transfer equation for multipolar interactions was derived according to the theory of Dexter and Reisfeld [31].

\[
\frac{\tau_{S0}}{\tau_S} \propto C^{\alpha/3}
\]

where \(C\) is the total concentration of Bi\(^{3+}\) and Eu\(^{3+}\) ions. \(\tau_S\) and \(\tau_{S0}\) represent the lifetime values of Eu\(^{3+}\)-doped and non-Eu\(^{3+}\)-doped, respectively. The values \(\alpha = 6, 8, 10\) indicate different types of dipole–dipole, dipole–quadrupole, and quadrupole–quadrupole interactions, respectively. As visualized in Figure 2d, the fitting factors of SLSO:0.06Bi\(^{3+}\), 0.05Eu\(^{3+}\) samples are equal to 0.899, 0.946, and 0.974 for \(\alpha = 6, 8, 10\), respectively, where \(R^2\) obtains the maximum at \(\alpha = 10\); hence, the energy transfer mechanism of Bi\(^{3+}\)-Eu\(^{3+}\) is quadrupole–quadrupole interaction.

Time-resolved photoluminescence (TRPL) spectroscopy reveals the dynamic behavior of doped ions with time in the emission spectrum, providing the ability to discriminate luminescent ions. Under the 350 nm Nano-LED lamp excitation, the TRPL spectra and fluorescence decay curves of SLSO:0.06Bi\(^{3+}\), 0.05Eu\(^{3+}\) are shown in Figure 3. Since the lifetimes of Bi\(^{3+}\) and Eu\(^{3+}\) are not on the corresponding level of magnitude, it can be noticed that the TRPL spectra of Bi\(^{3+}\) and Eu\(^{3+}\) do not appear at the same time in the coordinating system, as is visualized in Figure 3a,c. Figure 3b,d show the decay curves of Bi\(^{3+}\) and Eu\(^{3+}\) in SLSO:0.06Bi\(^{3+}\), 0.05Eu\(^{3+}\), respectively, and the lifetimes are calculated as follows [32–35]:

\[
I(t) = A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2)
\]

where \(t\) represents the decay time, \(\tau_1\) represents the fast decay lifetime, and \(\tau_2\) represents the slow decay lifetime. The average lifetime of the activated ion \(\tau_{av}\) can be expressed by the following equation:

\[
\tau_{av} = (A_1 \tau_1^2 + A_2 \tau_2^2) / (A_1 \tau_1 + A_2 \tau_2)
\]

The lifetimes of Bi\(^{3+}\) decrease from 473.2 to 65.3 ns with increasing Eu\(^{3+}\) concentration, while the lifetime of Eu\(^{3+}\) increases sustainably from 376.7 to 573.4 µs. This means there is an energy transfer from Bi\(^{3+}\) to Eu\(^{3+}\).

As shown in Figure 4a, when \(y\) is at 0.15Eu\(^{3+}\), energy transfer efficiency can reach 86.2%, and its value increases continuously with increasing Bi\(^{3+}\) concentration. This is because the emission peak of Bi\(^{3+}\) has an overlapping region with the excitation peak of Eu\(^{3+}\) to promote radiation reabsorption progress and, hence, energy transfer efficiency. Figure 4b illustrates the energy level diagram of Bi\(^{3+}\) and Eu\(^{3+}\) in SLSO. Figure 4c depicts the Commission International de L’Eclairage (CIE) chromaticity coordinates of SLSO:0.06Bi\(^{3+}\), 0.05Eu\(^{3+}\). Obviously, SLSO: 0.06Bi\(^{3+}\), 0.05Eu\(^{3+}\) can emit yellow and red light, and the CIE values are from (0.377, 0.483) to (0.590, 0.376) with increasing concentrations of Eu\(^{3+}\).
Figure 2. (a) Excitation and emission spectra of SLSO:0.06Bi$^{3+}$, 0.05Eu$^{3+}$; (b) emission spectra of SLSO:0.06Bi$^{3+}$, yEu$^{3+}$ ($\lambda_{\text{ex}} = 350$ nm); (c) Emission intensities of SLSO:0.06Bi$^{3+}$, yEu$^{3+}$ ($\lambda_{\text{em}} = 550$ and 615 nm); (d) relationship between $\tau_{S0}/\tau_0$ with $C^{6/3}$, $C^{8/3}$, and $C^{10/3}$.

Time-resolved photoluminescence (TRPL) spectroscopy reveals the dynamic behavior of doped ions with time in the emission spectrum, providing the ability to discriminate luminescent ions. Under the 350 nm Nano-LED lamp excitation, the TRPL spectra and fluorescence decay curves of SLSO:0.06Bi$^{3+}$, 0.05Eu$^{3+}$ are shown in Figure 3. Since the lifetimes of Bi$^{3+}$ and Eu$^{3+}$ are not on the corresponding level of magnitude, it can be noticed that the TRPL spectra of Bi$^{3+}$ and Eu$^{3+}$ do not appear at the same time in the coordinating system, as is visualized in Figure 3a, c. Figure 3b, d show the decay curves of Bi$^{3+}$ and Eu$^{3+}$ in SLSO:0.06Bi$^{3+}$, yEu$^{3+}$, respectively, and the lifetimes are calculated as follows [32–35]:

$$I(t) = A_1 \exp\left(-\frac{t}{\tau_1}\right) + A_2 \exp\left(-\frac{t}{\tau_2}\right)$$

(3)

where $t$ represents the decay time, $\tau_1$ represents the fast decay lifetime, and $\tau_2$ represents the slow decay lifetime. The average lifetime of the activated ion ($\tau_{\text{av}}$) can be expressed by the following equation:

$$\tau_{\text{av}} = \frac{A_1 \tau_1^2 + A_2 \tau_2^2}{A_1 \tau_1 + A_2 \tau_2}$$

(4)

The lifetimes of Bi$^{3+}$ decrease from 473.2 to 65.3 ns with increasing Eu$^{3+}$ concentration, while the lifetime of Eu$^{3+}$ increases sustainably from 376.7 to 573.4 μs. This means there is an energy transfer from Bi$^{3+}$ to Eu$^{3+}$.
Figure 3. (a,b) Time-resolved spectrum and fluorescence decay curve of Bi\(^{3+}\); (c,d) time-resolved spectrum and fluorescence decay curve of Eu\(^{3+}\) in SLSO: Bi\(^{3+}\), yEu\(^{3+}\).

3.3. Luminescence Properties of SLSO:0.06Bi\(^{3+}\), mMn\(^{4+}\)

To further increase the luminescence intensity in the red region, we chose MnO\(_2\) as the raw material to provide Mn\(^{4+}\) ion co-doped with Bi\(^{3+}\) ion for luminescence, which provides the basis for the preparation of white LEDs with a high color rendering index and a low correlated color temperature. Figure 5a,b show the emission and excitation spectra of SLSO: mMn\(^{4+}\) (m = 0.001, 0.003, 0.005, 0.007, 0.01, and 0.015). As the samples were prepared in air, it was speculated that the Mn ions were not reductive and we did not consider the red luminescence to be Mn\(^{2+}\). Secondly, most of the luminescence of Mn\(^{2+}\) is a green or red broadband spectrum, whereas the Mn luminescence is a narrow band from 650 to 800 nm in Figure 5a. Afterwards, to further figure out the Mn\(^{4+}\) luminescence center, we surveyed some published literature and found that the luminescence around 707 nm, with narrowband emissions, is that of Mn\(^{4+}\) ions. It can be seen that the excitation spectrum contains the 200–450 nm broadband, which is attributed to the charge migration band of Mn\(^{4+}\)-O\(^2-\) and the \(^4A_{2g}\)→\(^4T_{1g}\) energy level transition of Mn\(^{4+}\); the weaker excitation peak at 395 nm is ascribed to the \(^4A_{2g}\)→\(^2T_{2g}\) transition of Mn\(^{4+}\); the other excitation peaks at 450–600 nm are considered to be the \(^4A_{2g}\)→\(^4T_{2g}\) energy level transition. SLSO: mMn\(^{4+}\) presents the same spectral shape, and the emission intensity can reach a maximum at 0.007 Mn\(^{4+}\); there is a concentration quenching effect. Figure 5c shows that the emission spectra of SLSO: Bi\(^{3+}\), Mn\(^{4+}\) contain the emission peaks of Bi\(^{3+}\) and Mn\(^{4+}\), as shown in Figure 5d; with increasing Mn\(^{4+}\) concentrations, the emission intensities of Bi\(^{3+}\) decrease and the emission intensities of Mn\(^{4+}\) increase. This indicates that there may be an energy transfer from Bi\(^{3+}\) to Mn\(^{4+}\) in SLSO:0.06Bi\(^{3+}\), mMn\(^{4+}\). In our previous research, it was found that Bi\(^{3+}\) ions enter the lattice sites Sr1 and Sr2(La) in SLSO; however, in this paper, the radius of Mn\(^{4+}\) ions r = 0.67\(\AA\) (CN = 6) is similar to Sc\(^{3+}\) ion radius \(r = 0.745\(\AA\) (CN = 6),
which is suitable for Mn$^{4+}$ ions to dope into. Therefore, it is believed that Mn$^{4+}$ enters the [ScO$_6$] octahedron.

Figure 6a depicts the energy transfer process of Bi$^{3+}$ and Mn$^{4+}$, where the electrons were pumped to the excited states $^1P_1$ and $^3P_1$ from the ground state $^1S_0$ under 250 and 350 nm excitation, according to the 6S$_2$ outer-electron [36]. Meanwhile, the electrons on the ground state $^4A_{2g}$ of Mn$^{4+}$ were excited by the UV light source transition to the excited states $^4T_{1g}$, $^2T_{2g}$, and $^4T_{2g}$ [37]. Then, the electrons relaxed to the lowest excited states $^3P_1$ and $^2E_g$ and released photons to emit 550 and 707 nm light through the radiation process back to the ground state. The variation in the fluorescence lifetime of the sensitizer ions doped in the matrix is direct evidence that energy transfer occurs. Figure 6b presents the decay curves of SLSO: Bi$^{3+}$, mMn$^{4+}$. All decay curves can be well fitted to a double exponential function, and the lifetime values of Bi$^{3+}$ were 458.3, 426.4, 359.3, 250.4, 158.7, 123.2, and 97.8 ns. Moreover, the decay curves of Mn$^{4+}$ in SLSO:0.06Bi$^{3+}$, mMn$^{4+}$ were also measured, and the lifetime values of Mn$^{4+}$ increased from 12.4 to 57.5 µs, as displayed in Figure 6c. Moreover, the energy transfer efficiency can reach 78.60%, as shown in Figure 6d. In this process, although some energy is lost because of the non-radiative transition, it is clear that Bi$^{3+}$-Mn$^{4+}$ can still exhibit an efficient energy transfer, which is mainly attributed to the fact that Bi$^{3+}$ and Mn$^{4+}$ ions have not only the same excitation band but also the same radiative reabsorption process because the emission spectrum of Bi$^{3+}$ and the excitation spectrum of Mn$^{4+}$ have a large overlap region.

Figure 4. (a) Energy transfer efficiency of SLSO:0.06Bi$^{3+}$, yEu$^{3+}$; (b) schematic energy level diagram of Bi$^{3+}$ and Eu$^{3+}$ in SLSO; (c) color coordinates and luminescence photos of SLSO: Bi$^{3+}$, yEu$^{3+}$.
SLSO:0.06Bi³⁺, mMn⁴⁺. In our previous research, it was found that Bi³⁺-Mn⁴⁺ can still exhibit an efficient energy transfer, which is mainly attributed to the matrix is direct evidence that energy transfer occurs. Figure 6b presents the emission spectra of SLSO:0.007Mn⁴⁺. Excitation and emission spectra of SLSO:0.007Mn⁴⁺ (λex = 350 nm).

The energy transfer process may be caused by the exchange interaction or the multipole interaction; the former should be less than 5 Å, according to the critical distance ($R_c$). The $R_c$ value between Bi³⁺ and Mn⁴⁺ can be evaluated using Blasse’s theory [38], and the calculated $R_c$ is 17.31 Å. It is proposed that the energy transfer mechanism may be the electron multipole–multipole interaction. In addition, the Dexter theory and the Reisfeld approximation can be utilized to analyze the multipole interaction type of the energy transfer mechanism. The values $\alpha = 6, 8$, and 10 correspond to dipole–dipole, dipole–quadrupole, and quadrupole–quadrupole interactions, respectively. The plot of $\tau_{S0}/\tau_{S}$ and $C^{\alpha/3}$ was fitted linearly, and the results are shown in Figure 7. By comparing the coefficient of determination ($R^2$ value), the best fit was obtained for $\alpha = 6$, and the outcome clearly illustrates that the energy transfer from Bi³⁺ to Mn⁴⁺ in SLSO is primarily defined by electric dipole–dipole interaction. The Mn⁴⁺ ion can emit strong deep red light, which can be excited in near ultraviolet for the lighting equipment of plant growth.

Figure 5. (a) Excitation and emission spectra of SLSO:0.007Mn⁴⁺; (b) emission spectra of SLSO: mMn⁴⁺; (c) emission spectra of SLSO:0.06Bi³⁺, mMn⁴⁺ (λex = 350 nm); (d) the emission intensities of SLSO:0.06Bi³⁺, mMn⁴⁺ (λem = 550 and 707 nm).
Figure 6. (a) Schematic energy level diagram of Bi$^{3+}$/Mn$^{4+}$ in SLSO; (b) the decay curves of Bi$^{3+}$; (c) the decay curves of Mn$^{4+}$; (d) energy transfer efficiencies of SLSO:0.06Bi$^{3+}$, mMn$^{4+}$.

Figure 7. Relationship between $\tau_{S0}/\tau_0$ and (a) $C^{6/3}$, (b) $C^{8/3}$, and (c) $C^{10/3}$. 

The fact that Bi$^{3+}$ and Mn$^{4+}$ ions have not only the same excitation range from 400 to 1350 nm under the 350 nm excitation but also the same decay curves of Mn$^{4+}$ ions can be used to analyze the multipole interaction type of electron multipole. The values $\alpha$ and $\beta$ can be fitted approximately to analyze the multipole interaction type of electron multipole. The energy transfer process may be caused by the exchange interaction or the Förster mechanism. The Mn$^{4+}$ ions may be excited in near ultraviolet for the lighting equipment of plant growth.
3.4. Luminescence Properties of SLSO:0.06Bi\(^{3+}\), zYb\(^{3+}\)

In order to explore the possibility of near-infrared luminescence in SLSO, we co-doped Yb\(^{3+}\) with Bi\(^{3+}\). Figure 8a shows the emission spectra of SLSO:0.06Bi\(^{3+}\), zYb\(^{3+}\) (z = 0.01, 0.015, 0.02, 0.05, and 0.15), which can range from 400 to 1350 nm under the 350 nm excitation. Figure 8b depicts the excitation spectrum and the emission spectrum of SLSO:0.06Bi\(^{3+}\), 0.02Yb\(^{3+}\), and the 980 nm emission peak reaches the high excited state \(^2F_{7/2}\) to ground state \(^2F_{5/2}\) of the Yb\(^{3+}\) ions [39]; the 550 nm emission peak is due to the excited state \(^3P_1\) to ground state \(^1S_0\) of the Bi\(^{3+}\) ions. As shown in Figure 8c, obviously, with an increase in Yb\(^{3+}\) concentrations, the emission intensities of 980 nm increase and those of 550 nm decrease; it means there may be an energy transfer from Bi\(^{3+}\) to Yb\(^{3+}\). According to the critical distance (\(R_c\)) [40], for SLSO: Bi\(^{3+}\), Yb\(^{3+}\), \(N = 4, V = 683.702\ \AA^3\), and \(x_c = 0.11\), the critical distance is \(R_c = 14.37\ \AA\). The plot of \(\tau_0 / \tau_0\) and \(C^{\alpha/3}\) is fitted linearly in Figure 8d, where \(\alpha = 6, 8,\) and 10 corresponds to dipole–dipole (d–d), dipole–quadrupole (d–q), and quadrupole–quadrupole (q–q) interactions, respectively. The fitting factors of \(R^2\) are 0.957, 0.931, and 0.908, respectively, and the best fit was obtained for \(\alpha = 6\), showing that Bi\(^{3+}\) and Yb\(^{3+}\) belong to the d–d interaction.

Figure 8a depicts the energy transfer process of Bi\(^{3+}\), Yb\(^{3+}\) [41]. Figure 8b shows the decay curves of Bi\(^{3+}\) in SLSO: Bi\(^{3+}\), zYb\(^{3+}\), and the lifetime values were 512.2, 486.3, 481.0, 480.7, 437.6, and 371.3 ns. Obviously, the lifetime of Bi\(^{3+}\) ions gradually decayed, and Figure 9c presents the lifetime values of a Yb\(^{3+}\) increase from 374.1 to 558.1 μs, which means the energy transfer from Bi\(^{3+}\) ions to Yb\(^{3+}\) ions. The energy transfer efficiency was

![Figure 8](image_url)

Figure 8. (a) Emission spectra of SLSO: Bi\(^{3+}\), zYb\(^{3+}\); (b) excitation and emission spectra of SLSO: Bi\(^{3+}\), 0.02Yb\(^{3+}\); (c) emission intensities of SLSO:0.06Bi\(^{3+}\), zYb\(^{3+}\) (\(\lambda_{em} = 550\) and 980 nm); (d) relationship between \(\tau_0 / \tau_0\) and \(C^{\alpha/3}\) in SLSO:0.06Bi\(^{3+}\), zYb\(^{3+}\).
calculated as follows: \( \eta = 1 - \frac{\tau_0}{\tau} \) [42], and Figure 9d shows that the \( \eta \) value can reach a maximum of \( \eta = 27.5\% \) at \( z = 0.15 \). Since the excitation spectrum of Yb\(^{3+}\) ion is concentrated in the near-UV region and the emission spectrum of Bi\(^{3+}\) is in the visible region, they have fewer overlapping areas, so the energy transfer efficiency between them is low. However, it is found that the Bi\(^{3+}\)-Yb\(^{3+}\) co-doping greatly broadens the emission range; this means that SLSO: Bi\(^{3+}\), Yb\(^{3+}\) has a promising application in the visible illumination region as well as the near-infrared region.

**Figure 9.** (a) Schematic energy level diagram of Bi\(^{3+}\) and Yb\(^{3+}\) ions in SLSO; (b) decay curves of Bi\(^{3+}\); (c) decay curves of Yb\(^{3+}\); (d) energy transfer efficiencies of SLSO:0.06Bi\(^{3+}\), zYb\(^{3+}\).

**4. Conclusions**

In summary, a series of SLSO:0.06Bi\(^{3+}\), yEu\(^{3+}\), SLSO:0.06Bi\(^{3+}\), nMn\(^{4+}\), and SLSO:0.06Bi\(^{3+}\), zYb\(^{3+}\) was synthesized by the high-temperature solid-state method and could create tunable color emissions by the energy transfer from Bi\(^{3+}\) to Eu\(^{3+}\)/Mn\(^{4+}\)/Yb\(^{3+}\), which was proven by the decay curves, time-resolved spectra, and spectral properties. The experiments have not only discussed the process of energy transfer from Bi\(^{3+}\) ions to other luminescent centers but have also investigated the interactions between the sensitized and activated ions. Based on the above studies, we believe that a large overlapping area between the emission spectrum of the sensitizer and the excitation spectrum of the activator will result in high energy transfer efficiency. Therefore, in order to prepare multifunctional luminescent materials with both visible and near-infrared emissions, the intense luminescence of the Yb\(^{3+}\) ion needs to be improved so that the emission spectrum of Bi\(^{3+}\) can be modulated to blue-
shift to get more overlapping regions in the future in order to obtain efficient energy transfer progress between Bi$^{3+}$ and Yb$^{3+}$, which can provide a novel tunable wavelength luminescent material for high-quality lighting and detection applications.

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**References**

1. Song, Y.; Guo, N.; Li, J.; Xin, Y.; Lü, W.; Miao, Y. Dual-emissive Ln$^{3+}$/Mn$^{4+}$ Co-doped double perovskite phosphor via site-beneficial occupation. *Mater. Adv.* 2021, 2, 1402–1412. [CrossRef]

2. Wang, W.; Yang, H.; Fu, M.; Zhang, X.; Guan, M.; Wei, Y.; Lin, C.C.; Li, G. Superior thermally-stable narrow-band green emitter from Mn$^{2+}$-doped zero thermal expansion (ZTE) material. *Chem. Eng. J.* 2021, 415, 128979. [CrossRef]

3. Yuan, L.; Jin, Y.; Xiong, G.; Wu, H.; Li, J.; Liu, H.; Chen, L.; Hu, Y. Flux-assisted low-temperature synthesis of Mn$^{4+}$-doped unusual broadband deep-red phosphors toward warm w-LEDs. *J. Alloys Compd.* 2021, 870, 159394. [CrossRef]

4. Lin, Y.; Wang, G.-E.; Li, L.; Hu, C.-L.; Lin, S.; Mao, J.-G. Rare-Earth-Free Barium Borostannate with Deep-Blue Light Emission. *Chem. Mater.* 2021, 33, 1852–1859. [CrossRef]

5. Zhang, T.; Wu, Y.; Ma, X. Tunable multicolor room-temperature phosphorescence including white-light emission from amorphous copolymers. *Chem. Eng. J.* 2021, 412, 128689. [CrossRef]

6. Li, K.; Shang, M.; Lian, H.; Lin, J. Recent development in phosphors with different emitting colors via energy transfer. *J. Mater. Chem. C* 2016, 4, 5507–5530. [CrossRef]

7. Yuan, B.; Huang, Y.; Yu, Y.M.; Seo, H.J. Luminescence and structure of Eu$^{2+}$-doped Ba$_2$CaMg$_2$Si$_6$O$_{17}$. *Ceram. Int.* 2012, 38, 2219–2223. [CrossRef]

8. Yu, R.; Zhong, S.; Xue, N.; Li, H.; Ma, H. Synthesis, structure, and peculiar green emission of NaBaBO$_3$:Ce$^{3+}$ phosphors. *Dalton Trans.* 2014, 43, 10969–10976. [CrossRef]

9. Li, J.; Liu, J.; Yu, X. Synthesis and luminescence properties of Bi$^{3+}$-doped YVO$_4$ phosphors. *J. Alloys Compd.* 2011, 509, 9897–9900. [CrossRef]

10. Guo, C.; Ding, X.; Luan, L.; Xu, Y. Two-color emitting of Eu$^{2+}$ and Mn$^{2+}$ co-doped Sr$_2$Mg$_3$P$_2$O$_{15}$ for UV LEDs. *Sens. Actuators B Chem.* 2010, 143, 712–715. [CrossRef]

11. Maggay, I.V.B.; Lin, P.-C.; Liu, W.-R. Enhanced luminescence intensity of novel red-emitting phosphor-Sr$_3$Lu$_2$(BO$_3$)$_4$:Bi$^{3+}$,Eu$^{3+}$ via energy transfer. *J. Solid State Light* 2014, 1, 13. [CrossRef]

12. Xue, J.; Yu, Z.; Noh, H.M.; Lee, B.R.; Choi, B.C.; Park, S.H.; Jeong, J.H.; Du, P.; Song, M. Designing multi-mode optical thermometers via the thermochromic LaNbO$_4$:Bi$^{3+}$/Ln$^{3+}$ (Ln = Eu, Tb, Dy, Sm) phosphors. *Chem. Eng. J.* 2021, 415, 128977. [CrossRef]

13. Liu, D.; Yun, X.; Li, G.; Dong, P.; Molokeev, M.S.; Lian, H.; Shang, M.; Lin, J. Enhanced Cyan Emission and Optical Tuning of Ca$_3$Ga$_4$O$_8$:Bi$^{3+}$ for High-Quality Full-Spectrum White Light-Emitting Diodes. *Adv. Opt. Mater.* 2020, 8, 2001037. [CrossRef]

14. Zhang, Y.; Chen, D.; Wang, W.; Yan, S.; Liu, J.; Liang, Y. Long-lasting ultraviolet-A persistent luminescence and photo stimulated persistent luminescence in Bi$^{3+}$-doped LiScGeO$_4$ phosphor. *Inorg. Chem. Front.* 2020, 7, 3063–3071. [CrossRef]

15. Xiong, P.; Li, Y.; Peng, M. Recent Advances in Super Broad Infrared Luminescence Bismuth-Doped Crystals. *iScience* 2020, 23, 101578. [CrossRef]

16. Yang, X.; Zhao, L.; Lui, Z.; Tian, S.; Zhang, H.; Xu, X.; Qiu, J.; Yu, X. Achieving high thermal stability of different rare-earth ions in a single matrix host via the manipulation of the local structure by a solid solution. *Phys. Chem. Chem. Phys.* 2020, 22, 16294–16300. [CrossRef]

17. de Weerd, C.; Gomez, L.; Zhang, H.; Buma, W.J.; Nederelu, G.; Kovaleiko, M.V.; Gregorkiewicz, T. Energy Transfer between Inorganic Perovskite Nanocrystals. *J. Phys. Chem. C* 2016, 120, 13310–13315. [CrossRef]

18. Bredas, J.-L.; Beljonne, D.; Coropceanu, V.; Cornil, J. Charge-Transfer and Energy-Transfer Processes in $\pi$-Conjugated Oligomers and Polymers: A Molecular Picture. *Chem. Rev.* 2004, 104, 4971–5004. [CrossRef]

19. Powell, R.C.; Soos, Z.G. Singlet exciton energy transfer in organic solids. *J. Lumin.* 1975, 11, 1–45. [CrossRef]

20. Zhou, L.; Chen, Y.; Shen, Y.; Lin, J.; Fu, J.; Lei, L.; Ye, R.; Deng, D.; Xu, S. Designing Optical Thermometers Using Down/Up conversion Ca$_{12}$Al$_{10}$Zn$_6$O$_{35}$: Ti$^{4+}$, Eu$^{3+}$/Yb$^{3+}$, Er$^{3+}$ Thermosensitive Phosphors. *Inorg. Chem.* 2022, 61, 10667–10677. [CrossRef]
21. Ji, R.; Seto, T.; Liu, W.; Wang, Y. Broadband Yellow Phosphor Discovered by Single-Particle Analysis Based on Fluorescence Microscopy, Scanning Electron Microscopy, Cathodoluminescence, and Energy-Dispersive X-ray Spectroscopy. *J. Phys. Chem. A* 2022, 126, 4647–4656. [CrossRef] [PubMed]

22. Nanda, S.S.; Nayak, P.; Gupta, S.K.; Rawat, N.S.; Goutam, U.K.; Dash, S. Structural, optical spectroscopy and energy transfer features of Tb\(^{3+}\)-activated (Y, Gd)\(_4\)F\(_9\) nanophosphors for UV-based LEDs. *New J. Chem.* 2022, 46, 15617–15627. [CrossRef]

23. Zu, X.-G.; Wang, Y.; Wei, L.; Lv, X.-S.; Fu, Y.-B.; Li, J.; Zhang, Y.-Y.; Wang, X.-P.; Liu, B.; Yang, Y.-G. Luminescence properties and energy transfer of La\(_2\)Gd\(_3\)SiO\(_{14}\):Eu\(^{3+}\), Tb\(^{3+}\) phosphors. *Crystral. Eng. Comm.* 2021, 23, 4194–4204. [CrossRef]

24. Huang, A.; Yang, Z.; Yu, C.; Chai, Z.; Qiu, J.; Song, Z. Tunable and white light emission of a single-phased Ba\(_2\)Y(BO\(_3\))\(_3\):Cl: Bi\(^{3+}\), Eu\(^{3+}\) phosphor by energy transfer for ultraviolet converted white LEDs. *J. Phys. Chem. C* 2017, 121, 5267–5276. [CrossRef]

25. Hao, Z.; Zhang, J.; Zhang, X.; Wang, X. CaSc\(_2\)O\(_4\):Eu\(^{3+}\): A tunable full-color emitting phosphor for white light emitting diodes. *Opt. Mater.* 2011, 33, 355–358. [CrossRef]

26. Xin, S.; Wang, Y.; Wang, Z.; Zhang, F.; Wen, Y.; Zhu, G. An Intense Red-Emitting Phosphor YBa\(_3\)(PO\(_4\))\(_3\):Eu\(^{3+}\) for Near-Ultraviolet Light Emitting Diodes Application. *Electrochem. Solid-State Lett.* 2011, 14, H438–H441. [CrossRef]

27. Meng, Q.; Zhang, H.; Fu, L. Structural changes of TiO\(_2\) gel using Eu\(^{3+}\) ion as the fluorescence probe. *J. Inorg. Mater.* 1999, 14, 630–634.

28. Cao, R.; Xiao, H.; Zhang, F.; Cheng, X.; Su, L.; Xiao, F.; Luo, Z.; Chen, T. Synthesis, energy transfer, charge compensation and luminescence properties of CaZrO\(_2\): Eu\(^{3+}\), Bi\(^{3+}\), Li\(^+\) phosphor. *J. Mater. Sci. Mater. Electron.* 2019, 30, 2327–2333. [CrossRef]

29. Tang, Z.; Jiang, L.; Yang, J.; Tang, J.; Wu, A. Eu\(^{3+}\)-Activated Alkali Rare-Earth Double-Tungstate Nanoparticles for Near-Ultraviolet-Light-Triggered Indoor Illumination. *ACS Appl. Nano Mater.* 2022, 5, 9072–9083. [CrossRef]

30. Li, J.; Huang, J.; Jiang, P.; Gao, W.; Cong, R.; Yang, T. Complex crystal structure and photoluminescence of Bi\(^{3+}\)-doped and Bi\(^{3+}\)/Eu\(^{3+}\) co-doped Ca\(_2\)Mg\(_2\)Ga\(_3\)O\(_{18}\). *Dalton Trans.* 2021, 50, 6848–6856. [CrossRef]

31. Zheng, B.; Zhang, X.; Zhang, D.; Wang, F.; Zheng, Z.; Yang, X.; Yang, Q.; Song, Y.; Zou, B.; Zou, H. Ultra-wideband phosphor Mg\(_2\)Gd\(_3\)(SiO\(_4\))\(_2\):Ce\(^{3+}\), Mn\(^{4+}\): Energy transfer and pressure-driven color tuning for potential applications in LEDs and pressure sensors. *Chem. Eng. J.* 2022, 427, 131897. [CrossRef]

32. Huang, D.; Deng, P.; Lian, H.; Zeng, Q.; Lin, J. Luminescence and energy-transfer properties in Bi\(^{3+}\)/Mn\(^{4+}\)-codoped Ba\(_2\)GdNbO\(_6\) double-perovskite phosphors for white-light-emitting diodes. *Inorg. Chem.* 2019, 58, 15507–15519. [CrossRef]

33. Ding, J.; Kuang, M.; Liu, S.; Zhang, H.; Huo, J.; Ni, H.; Zhang, Q.; Li, J. Sensitization of Mn\(^{4+}\) luminescence via efficient energy transfer to suit the application of high color rendering WLEDs. *Dalton Trans.* 2022, 51, 9501–9510. [CrossRef]

34. Rastogi, C.K.; Sharma, S.K.; Sasmal, S.; Pala, R.G.S.; Kumar, J.; Sivakumar, S. Terbium Ion-Mediated Energy Transfer in WO\(_3\):Tb\(^{3+}\) and Eu\(^{3+}\) Phosphors for UV-Sensitized White Light Emission. *J. Phys. Chem. C* 2021, 125, 6163–6175. [CrossRef]

35. Awater, R.H.P.; Dorenbos, P. Towards a general concentration quenching model of Bi\(^{3+}\) luminescence. *J. Lumin.* 2017, 188, 487–489. [CrossRef]

36. Li, Z.-J.; Liu, B.; Zhang, Y.-Y.; Zhang, N.-N.; Shi, Q.; Wei, L.; Yu, H.-J.; Fu, Y.-B.; Li, Q.-G.; Yang, Y.-G. Compounds, Cyan, deep red and white light emission generated by SrLaGa\(_3\)O\(_7\):Bi\(^{3+}\), SrLaGa\(_3\)O\(_7\):Mn\(^{4+}\) and SrLaGa\(_3\)O\(_7\):Bi\(^{3+}\)/Mn\(^{4+}\) phosphors. *J. Alloys Compd.* 2022, 894, 162455. [CrossRef]

37. Huang, D.; Deng, P.; Wei, Y.; Bai, B.; Lian, H.; Zeng, Q.; Lin, J. A deep-red-emitting Bi\(^{3+}\)/Mn\(^{4+}\)-codoped Ca\(_2\)Li\(_2\)Nb\(_2\)O\(_12\) phosphor: Luminescence and energy transfer properties. *Mater. Res. Bull.* 2020, 124, 110743. [CrossRef]

38. Zhou, R.; Kou, Y.; Wei, X.; Duan, C.; Chen, Y.; Yin, M. Broadband down conversion based near-infrared quantum cutting via cooperative energy transfer in YNbO\(_4\):Bi\(^{3+}\), Yb\(^{3+}\) phosphor. *Appl. Phys. B* 2012, 107, 483–487. [CrossRef]

39. Luo, H.; Zhang, S.; Mu, Z.; Wu, F.; Nie, Z.; Zhu, D.; Feng, X.; Zhang, Q. Near-infrared quantum cutting via energy transfer in Bi\(^{3+}\), Yb\(^{3+}\) co-doped Lu\(_2\)Ge\(_2\)O\(_7\) down-converters phosphor. *J. Alloys Compd.* 2019, 784, 611–619. [CrossRef]

40. Fujita, K.; Watanabe, R.; Iso, Y.; Isobe, T. Preparation and characterization of Y\(_2\)O\(_3\):Bi\(^{3+}\), Yb\(^{3+}\) nanosheets with wavelength conversion from near-ultraviolet to near-infrared. *J. Lumin.* 2018, 198, 243–250. [CrossRef]

41. Yadav, R.V.; Yadav, R.S.; Bahadur, A.; Singh, A.K.; Rai, S.B. Enhanced quantum cutting via Li\(^{3+}\) doping from a Bi\(^{3+}\)/Yb\(^{3+}\)-codoped gadolinium tungstate phosphor. *Inorg. Chem.* 2016, 55, 10928–10935. [CrossRef] [PubMed]