Intense 1.85 μm emission of Tm^{3+} sensitized by Mn^{4+} in $\text{Mn}^{4+}/\text{Tm}^{3+}$ co-doped $\text{Ca}_{14}\text{Zn}_6\text{Al}_{10}\text{O}_{35}$ phosphor

Wei Li, Xuejun Gao, Xiaoliang Yang, Xiangliang Jin and Siguo Xiao *

School of Physics and Optoelectronics & Institute for Nanophysics and Rare-earth

Luminescence, Xiangtan University, Hunan 411105, China

*Author to whom correspondence should be addressed. Electronic mail:

xiaosiguo@xtu.edu.cn

Abstract

$\text{Mn}^{4+}/\text{Tm}^{3+}$ co-doped $\text{Ca}_{14}\text{Zn}_6\text{Al}_{10}\text{O}_{35}$ near infrared phosphor is prepared with a sol-gel method and intense 1.85 μm emission of Tm^{3+} sensitized by Mn^{4+} is observed for the first time. The intense and broad excitation band of Mn^{4+} (250-550 nm) and efficient $\text{Mn}^{4+} \rightarrow \text{Tm}^{3+}$ energy transfer make the 1.85 μm emission very convenient to be obtained by pumping with light in a wide-wavelength region, especially with commercial GaN LEDs. The mechanisms for the $\text{Mn}^{4+} \rightarrow \text{Tm}^{3+}$ and Tm^{3+} - Tm^{3+} interaction have been discussed based on the Mn^{4+} and Tm^{3+} concentration dependent steady-state and transient spectral properties. It is found that both the $\text{Mn}^{4+} \rightarrow \text{Tm}^{3+}$ sensitization and the Tm^{3+} - Tm^{3+} inter-action are helpful to the improvement of the near infrared luminescence, resulting in the 1.85 μm emission for the $\text{Mn}^{4+}/\text{Tm}^{3+}$ co-doped phosphor 24 times of enhancement under excitation of 455 nm light as compared with that for the Mn^{4+} absent sample.

Keywords: 1.85 μm emission, $\text{Mn}^{4+}/\text{Tm}^{3+}$ co-doped, sensitization, infrared phosphor

1. Introduction

The luminescence materials doped with rare earth ions emitting at $\sim 2\ \mu\text{m}$ has been aroused extensive attention over the past decades due to the potential applications in the eye-safe laser, non-invasive medical diagnostics, atmospheric pollution monitoring, remote sensing, and optical pump sources [1-6]. Among the rare earth ions, Tm^{3+} might be an ideal activator because its emission wavelength generated by the $^3\text{F}_4 \rightarrow ^3\text{H}_6$ transition locates at $1.85\ \mu\text{m}$, very close to $2\ \mu\text{m}$. However, Tm^{3+} doped phosphors usually exhibits weak and narrow line-like absorption in the visible and near infrared (NIR) spectral ranges owing to the 4f-4f forbidden transitions. This results in its low excitation efficiency and correspondingly the weak $1.85\ \mu\text{m}$ emission. Sensitization is an important approach to enhance the absorption efficiency of Tm^{3+} and thus increase $1.85\ \mu\text{m}$ emission intensity. In past years, several sensitizers such as Cr^{3+} , Yb^{3+} have been attempted to improving the NIR emission of Tm^{3+} in different matrices and the enhancement of the $1.85\ \mu\text{m}$ emission by sensitization has been witnessed [6-12]. However, there still exist some disadvantages for these sensitizers. For instance, the sensitization efficiency of Cr^{3+} [6,8] is relatively low and thus could not bring about satisfactory improvement for Tm^{3+} emission in near infrared region, while Yb^{3+} ions do not always play a positive role because of the intense up-conversion emissions at 480 and 800 nm generated by the strong excited state absorption in the $\text{Tm}^{3+}/\text{Yb}^{3+}$ co-doped system [6,13]. Thus, it is still desirable to search more efficient sensitizer for Tm^{3+} to enhance its near infrared emission.

It is known that Mn^{4+} ions occupying octahedral sites usually show broad and

strong absorption spanning from 300 to 600 nm and emits light between 600 and 760 nm [14-23]. Efficient emission of Mn^{4+} has been observed in many kinds of matrixes with octahedral structure such as K_2SiF_6 , K_2GeF_6 , $\text{CaAl}_{12}\text{O}_{19}$, $\text{La}_2\text{MgGeO}_6$, $\text{CaMg}_2\text{Al}_{16}\text{O}_{27}$ and $\text{Ca}_{14}\text{Zn}_6\text{Al}_{10}\text{O}_{35}$ (CZAO) [24-30]. Among these matrixes, CZAO is especially attractive not only because it exhibits strong emission in the range of 650-700 nm, with a quantum efficiency approaching 50% [29], but also because of the excellent chemical and thermal stability [30].

In CZAO, Al^{3+} sites are going to be replaced by Mn^{4+} because Al^{3+} and Mn^{4+} ions have similar ion radius [26,31]. On the other hand, the Ca^{2+} sites could be replaced by Tm^{3+} because Ca^{2+} and Tm^{3+} ions also have similar ion radius (Ca^{2+} : $r = 1.0 \text{ \AA}$; Tm^{3+} : $r = 0.088 \text{ \AA}$) when a small amount of Tm^{3+} ions are introduced. Considering of the different valences of Ca^{2+} and Tm^{3+} , charge compensations are required. It was usually believed that the formative Ca^{2+} vacancies can compensate charge imbalance [32,33]. When Tm^{3+} ions are co-doped into CZAO, the Ca^{2+} vacancies might form and they could keep the electroneutrality of the compound. What's more, the intense emission band of ^2E level of Mn^{4+} locates around 700 nm, meaning the small energy mismatch between the $^2\text{E}(\text{Mn}^{4+})$ and $^3\text{F}_{2,3}(\text{Tm}^{3+})$ levels in CZAO matrix. Therefore, efficient energy transfer from Mn^{4+} to Tm^{3+} ions and efficient $1.85 \text{ }\mu\text{m}$ emission of Tm^{3+} by sensitization are possible. Additionally, the broad excitation band of Mn^{4+} in the 250-550 nm range with excitation peak at 460 nm makes the phosphor convenient to be pumped with a commercial GaN LED. In this work, therefore, the $1.85 \text{ }\mu\text{m}$ emission of Tm^{3+} and energy transfer mechanism

between Mn^{4+} and Tm^{3+} in CZA matrix have been investigated.

2. Experimental

The samples were prepared by the conventional sol-gel method. The raw materials were $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (99.9%), $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (99.9%), $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (99.9%), $\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (99.9%), $\text{Tm}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (99.9%) and $\text{C}_6\text{H}_8\text{O}_7 \cdot \text{H}_2\text{O}$ (99.9%). Firstly, each reagent was dissolved in distilled water with the stoichiometric ratio of $\text{Ca}_{14-x}\text{Zn}_6\text{Al}_{10-y}\text{O}_{35} \cdot \text{Mn}_y\text{Tm}_x$ ($x = 0.0, 0.05, 0.1, 0.2, 0.5, 0.6, 0.8, 1.0$, and $y = 0.0, 0.15, 0.3, 0.5, 0.6, 1.0$) and thoroughly mixed by stirring. Then $\text{C}_6\text{H}_8\text{O}_7$ aqueous solution was dripped into the nitrate solution with constant stirring with metal cation: $\text{C}_6\text{H}_8\text{O}_7 = 1:1.5$. After standing for 24 h, the solutions were drying at 200 °C to obtain precursors. The firing process involved two steps. First, presintering for the dried precursors was carried out to remove the organic matter by firing at 500 °C for 2h and then cooled to room temperature. After grinding, the powders were fired to 1000 °C at a heating rate of 6 °C/min in air and calcined at that temperature for 2 h to obtain the final samples.

The synthesized particles were identified by X-ray diffraction (XRD) on a Bruker D8 advanced equipment using Cu tube with Cu/K ($k = 0.1541$ nm) radiation. The morphology of the synthesized samples was characterized using a JSM-6610 scanning electron microscope (SEM). The excitation spectra and visible-near-infrared photoluminescence (PL) spectra were measured with a monochromator (Zolix Instrument, Omni- λ 320i) coupled with photomultiplier (PMTH-S1-CR131) and NIR sensitive detector (DInGaAs 2600-TE), in which a monochromator (Zolix Instrument

Omni-λ320) coupled with a 150W xenon lamp was used to provide the monochromatic exciting light. The luminescence decay curves of 714 nm were measured by a PTI QM 40 spectrofluorometer using a pulse xenon lamp as the excitation source. The NIR luminescence decay curves of 800 nm, 1.47 μm and 1.85 μm NIR emission were measured by a FLS920 (Edinburgh) spectrometer. All the measurements were carried out at room temperature.

3. Results and discussion

Fig. 1 portrays the XRD patterns of the synthesized samples $\text{Ca}_{14-x}\text{Zn}_6\text{Al}_{9.85}\text{O}_{35}:\text{Mn}_{0.15},\text{Tm}_x$ fired at 1000 °C for 2 h. As a reference, the XRD patterns of CZAO from the Inorganic Crystal Structure Database (ICSD No.87-0265) are also shown. The diffraction peaks of the as-prepared products can all be assigned to a pure CZAO cubic phase as the Tm^{3+} concentration is not more than $x = 0.5$. No other impurity phases appear when $x < 0.5$, indicating that almost all of the additive Mn^{4+} and Tm^{3+} ions were successfully incorporated into the Al^{3+} and Ca^{2+} ions sites, respectively. As the Tm^{3+} concentration is further increased ($x > 0.5$), however, weak CaTmAlO_4 peaks are found. The CZAO has a cubic symmetry cell with space group F23. The cell parameters of the doped CZAO were calculated using the XRD data. The inset in Fig. 1 gives the lattice parameter (a) and the unit cell volume as a function of Tm^{3+} concentration. It can be seen that the lattice parameter and unit cell volume slightly increase with Tm^{3+} concentration increasing, indicating that the lattice contraction originating from the substitution of Ca^{2+} (ionic radius = 1.0 Å) by Tm^{3+} with smaller ionic radius (0.88 Å) is over compensated by the lattice expansion caused by the

repulsion of the interstitial O^{2-} [34,35]. The microstructure of the $Ca_{13.5}Zn_6Al_{9.85}O_{35}:Mn_{0.15},Tm_{0.5}$ powder characterized by SEM is shown in the Fig. 2. It is clearly seen that the samples are composed of aggregated rod-shaped particles with average diameter of 0.8 μm and length of 2 μm .

Fig. 3 shows the excitation spectra of the Mn^{4+} single doped sample monitored at 714 nm and the Mn^{4+}/Tm^{3+} co-doped sample monitored at 1.85 μm , respectively. Broad excitation bands from 250 nm to 550 nm can be observed in both samples. The excitation bands at 360 nm and 455 nm originate in the $^4A_2 \rightarrow ^4T_1$ and $^4A_2 \rightarrow ^4T_2$ spin-allowed transitions of Mn^{4+} , respectively [30]. It is interesting to find that the excitation spectra monitored at 1.85 μm of Tm^{3+} emission in Mn^{4+}/Tm^{3+} co-doped sample is similar with that monitored at 714 nm of Mn^{4+} emission in Mn^{4+} single doped sample. This clearly proves that an energy transfer from Mn^{4+} to Tm^{3+} takes place when Mn^{4+} ion is excited in the Mn^{4+}/Tm^{3+} co-doped phosphor. The $Mn^{4+} \rightarrow Tm^{3+}$ energy transfer makes the 1.85 μm emission of Tm^{3+} easily to be obtained under excitation of light in wide wavelength range of 250-550 nm.

Fig. 4 (a) exhibits the emission spectra in range of 650-850 nm of Mn^{4+} , Tm^{3+} single doped and Mn^{4+}/Tm^{3+} co-doped phosphors with different concentrations of Tm^{3+} excited at 455 nm light, which is recorded with the photomultiplier. The Mn^{4+} single doped phosphor shows a strong deep red emission band with the highest peak at 714 nm, which is imputed to its $^2E \rightarrow ^4A_2$ transition. When a small amount of Tm^{3+} ions are added into the Mn^{4+} doped sample, the Mn^{4+} emission decreases and the characteristic emission band at 800 nm corresponding to the $^3H_4 \rightarrow ^3H_6$ transition of Tm^{3+} appears.

With the Tm^{3+} content increasing, the emission intensity of Mn^{4+} monotonously declines while the 800 nm emission of Tm^{3+} increases at first and then decreases after it reaches to a maximum value at $x=0.1$. Fig. 4(b) presents the NIR emission spectra in the range of 1350-2000 nm of Tm^{3+} single doped and $\text{Mn}^{4+}/\text{Tm}^{3+}$ co-doped phosphors as a function of Tm^{3+} concentration excited at 455 nm light recorded with the DInGaAs 2600 detector. In the $\text{Mn}^{4+}/\text{Tm}^{3+}$ co-doped phosphors there are two well-known emission bands centered at 1.47 μm and 1.85 μm associated with the transition of $^3\text{H}_4 \rightarrow ^3\text{F}_4$ and $^3\text{F}_4 \rightarrow ^3\text{H}_6$ of Tm^{3+} , respectively. As seen from the insets in fig. 4(a) and 4(b), Tm^{3+} -content-dependent luminescence behavior at 1.47 μm is similar with that at 800 nm. The reason lies in that 800 nm and 1.47 μm emissions both originate from states $^3\text{H}_4$. However, the Tm^{3+} -content-dependent emission behavior at 1.85 μm originating from the $^3\text{F}_4$ level is slightly different from those at 1.47 μm and 800 nm. As the Tm^{3+} doped content is higher than $x=0.1$, the luminescence intensity of 1.47 μm gradually decreases while the 1.85 μm emission still increases. The optimal Tm^{3+} doped content for 1.85 μm emission is found at $x = 0.5$ and the concentration quenching occurs when $x > 0.5$. Additionally, the emission spectra of $\text{Mn}^{4+}/\text{Tm}^{3+}$ co-doped sample pumped at 360 nm have also been measured, shown in the Fig. 4 (c) and (d). It is found that the emission spectra of the $\text{Mn}^{4+}/\text{Tm}^{3+}$ co-doped sample pumped at 360 nm are similar to those pumped at 455 nm. Moreover, the Tm^{3+} -concentration dependence of emission intensity pumped at 360 nm is also similar to that pumped at 455 nm.

At the optimal concentration of Tm^{3+} for 1.85 μm emission ($x=0.5$), the intensity

of the Tm^{3+} at 1.85 μm can be further enhanced by increasing Mn^{4+} content and the strongest emission appears at $y=0.5$, just as show in Fig. 5. Comparing with the Mn^{4+} absent sample, the luminescence intensity of 1.85 μm at the optimal doping concentration of Mn^{4+} and Tm^{3+} is enhanced by a factor of about 24. This indicates the energy transfer sensitization from Mn^{4+} to Tm^{3+} is quite efficient. At higher Mn^{4+} doped contents, however, the concentration quenching also occurs and the 1.85 μm emission intensity begins to decrease.

According to the excitation and emission properties of the Mn^{4+} single doped $\text{Mn}^{4+}/\text{Tm}^{3+}$ co-doped phosphors, an energy transfer sensitization mechanism is proposed and depicted in Fig. 6. Under excitation of 455 nm light, Mn^{4+} ions are initially excited from $^4\text{A}_2$ ground state to the $^4\text{T}_2$ excited state. Then the ions at $^4\text{T}_2$ states relax to their ^2E level non-radiatively and transfer their energy to the adjacent Tm^{3+} in the ground state ($^3\text{H}_6$) by the ET process ($\text{Mn}^{4+}: ^4\text{T}_2 + \text{Tm}^{3+}: ^3\text{H}_6 \rightarrow \text{Mn}^{4+}: ^4\text{A}_2 + \text{Tm}^{3+}: ^3\text{F}_{2,3}$), exciting Tm^{3+} ions to their $^3\text{F}_{2,3}$ state. After that, Tm^{3+} ions on the $^3\text{F}_{2,3}$ state rapidly nonradiatively decay to the $^3\text{H}_4$ state. The followed radiative transition $^3\text{H}_4 \rightarrow ^3\text{H}_6$ and $^3\text{H}_4 \rightarrow ^3\text{F}_4$ produce the 800 nm and 1.47 μm emission, respectively. On the other hand, Tm^{3+} ions at $^3\text{F}_4$ states can further radiatively decay down to their $^3\text{H}_6$ state, producing 1.85 μm emission.

It is worth noting that the Tm^{3+} - Tm^{3+} energy transfer is also beneficial to further increase the 1.85 μm emission. A cross relaxation process may take place through $\text{Tm}^{3+}: ^3\text{H}_4 + \text{Tm}^{3+}: ^3\text{H}_6 \rightarrow \text{Tm}^{3+}: ^3\text{F}_4 + \text{Tm}^{3+}: ^3\text{F}_4$ at high Tm^{3+} concentration, which weakens the 1.47 μm and in turn intensify the 1.85 μm emission. This can be

manifested by the different Tm^{3+} concentration dependent emission intensity at 1.47 μm and 1.85 μm , as shown in Fig. 4.

In order to better understand the energy-transfer sensitization mechanism, the luminescence decay curves of several transitions of Mn^{4+} and Tm^{3+} are measured with excitation at 455 nm. Fig. 7 (a) shows the luminescence decay curves monitored at 714 nm of Mn^{4+} . The average decay lifetimes of the emission at 714 nm can be obtained from the following equation [36]

$$\tau = \frac{\int_0^{\infty} t I(t) dt}{\int_0^{\infty} I(t) dt}, \quad (1)$$

Where $I(t)$ is the time dependent luminescence intensity at 714 nm. It is noticed that the average lifetime of Mn^{4+} decreases with the introduction of Tm^{3+} ions. With the Tm^{3+} content increasing from 0.0 to 1.0, the average decay lifetime of Mn^{4+} decreases from 1.088 to 0.212ms.

The energy-transfer efficiency η_T from the Mn^{4+} to Tm^{3+} ions in the $\text{CZAO:0.15Mn}^{4+}, x\text{Tm}^{3+}$ phosphors can be calculated by using the formula [37]

$$\eta_T = 1 - \tau/\tau_0, \quad (2)$$

where τ and τ_0 are the average decay lifetime of Mn^{4+} monitored at 714 nm, with and without Tm^{3+} doping, respectively. The η_T of $\text{CZAO:0.15Mn}^{4+}, x\text{Tm}^{3+}$ is calculated using Eq.(2) and η_T as a function of Tm^{3+} content is presented in the inset of Fig. 7(a). Although the value of η_T always increase with increasing Tm^{3+} dopant content in our experiment, the emission intensity of Tm^{3+} tends to decrease at higher Tm^{3+} content ($x>0.5$) due to the concentration quenching. The energy transfer efficiency is

59% in the CZAO:0.15Mn⁴⁺, 0.5Tm³⁺ sample with maximal 1.85 μm emission intensity.

The possible energy-transfer process between the Mn⁴⁺ and Tm³⁺ ions includes exchange interaction and multipolar interaction. It is known that if energy transfer takes place via exchange interaction, the critical distance between the sensitizer and activator should be shorter than 3-4 Å [38]. The critical distance R_c among the Mn⁴⁺ and Tm³⁺ ions can be calculated using the following equation [39]

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

Here V is the volume of the unit cell of Ca₁₄Zn₆Al₁₀O₃₅, x_c is the critical concentration, and N is the number of Ca²⁺ ions in the unit cell. In our case, N is 86, V is estimated to be 3286.7 Å³ and The critical concentration is about 0.0393 from the total concentration of the Mn⁴⁺ and Tm³⁺ ions at which the energy-transfer efficiency is 0.5. Therefore, according to the above equation, the critical distance (R_c) was calculated to be about 12.29 Å. This value is large than 3-4 Å, indicating little possibility of energy transfer via exchange interaction mechanism. Thus the electric multipolar interaction should be responsible for the energy transfer between the Mn⁴⁺ and Tm³⁺ ions. According to Dexter's energy-transfer expressions of multipolar interaction and Reisfeld's approximation, the following relation can be given [39-41]

$$\frac{\tau_0}{\tau} \propto C^{n/3}, \quad (4)$$

Where $n = 6, 8$ and 10 corresponding to dipole-dipole, dipole-quadrupole, and quadrupole-quadrupole interactions, respectively. C is the doping concentration of

the Tm^{3+} ions. The dependence of τ_0/τ of Mn^{4+} on $C^{n/3}$ is shown in Fig. 8. When $n = 6$ it shows a best linear relation with goodness of fit $R^2=0.99265$, implying that the dipole-dipole interaction predominantly performs the energy transfer from the Mn^{4+} to Tm^{3+} ions.

To know the properties of the Tm^{3+} - Tm^{3+} interaction, the luminescence decay curves of Tm^{3+} emission at 800 nm under excitation of 455 nm wavelength for co-doped (CZAO:0.15 Mn^{4+} , x Tm^{3+}) phosphors have been measured, presented in Fig.7 (b). It is found that an evident rise-up process in the early stage of the curve can be observed when the Tm^{3+} doped content is less than $x = 0.1$. This indicates that the energy transfer probability from Mn^{4+} to Tm^{3+} is larger than that the Tm^{3+} - Tm^{3+} cross relaxation interaction at low Tm^{3+} content, making the population of Tm^{3+} ion on $^3\text{H}_4$ state sustaining growth for a period of time when the 455 nm excitation light is stopped. However, once the Tm^{3+} content is further increased, the rise-up process is hardly observed. This may attributed to the rapid depopulation of the Tm^{3+} ions on $^3\text{H}_4$ state performed by the cross relaxation process $\text{Tm}^{3+}:^3\text{H}_4 + \text{Tm}^{3+}:^3\text{H}_6 \rightarrow \text{Tm}^{3+}:^3\text{F}_4 + \text{Tm}^{3+}:^3\text{F}_4$. It is also noted that the average lifetime of 800 nm emission decreases monotonously from 1.8702 to 0.3622ms, with the Tm^{3+} content increasing from 0.05 to 0.8. The decreased lifetime is also ascribed to the Tm^{3+} - Tm^{3+} interaction at high Tm^{3+} concentration. The luminescence decay curves of Tm^{3+} emission at 1.47 μm and 1.85 μm under excitation of 455 nm wavelength for co-doped (CZAO:0.15 Mn^{4+} , x Tm^{3+}) phosphors have been also measured, presented in Fig. 7 (c) and (d). Similarly, evident rise-up process in the early stage of the decay curves for both 1.47 μm and

1.85 μm can be observed when the Tm^{3+} doped content is less than $x = 0.1$. Once the Tm^{3+} content is further increased, the rise-up process almost disappears due to the increased Tm^{3+} - Tm^{3+} interaction. It is found that the 800 nm, 1.47 μm and 1.85 μm emissions present similar Tm^{3+} -concentration dependent decay properties since these emissions all originate in the radiative transitions of Tm^{3+} and rely on the energy transfer sensitization from Mn^{4+} to Tm^{3+} .

4. Conclusion

In summary, a novel 1.85 μm near infrared phosphor $\text{Ca}_{14}\text{Zn}_6\text{Al}_{10}\text{O}_{35}:\text{Mn}^{4+}, \text{Tm}^{3+}$ has been synthesized via a sol-gel method. The largely enhanced 1.85 μm emission of Tm^{3+} is attributed to Mn^{4+} - Tm^{3+} sensitization as well as the Tm^{3+} - Tm^{3+} interaction when pumped by 455 nm. It is believed that a dipole–dipole interaction is dominantly responsible for the energy transfer sensitization from Mn^{4+} to Tm^{3+} . The energy transfer efficiency is calculated to be 59% in the phosphor that gives the strongest emission at 1.85 μm with optimum Tm^{3+} doping concentration. The 1.85 μm emission in $\text{Ca}_{14}\text{Zn}_6\text{Al}_{10}\text{O}_{35}:\text{Mn}^{4+}, \text{Tm}^{3+}$ could be pumped with a commercial GaN LED, making this emission of wide application very convenient to be obtained.

Acknowledgments

This work was supported by the National Science Foundation of China (No. 51372214 & 61233010), Project of Department of science and technology of Hunan Province of China (No. 2014FJ3124), and the Open Project of State Key Laboratory of Rare Earth Resources Utilization, Changchun Institute of Applied Chemistry, Chinese Academy of Science (RERU2013017).

Figure captions

Fig. 1. XRD patterns of $\text{Ca}_{14-x}\text{Zn}_6\text{Al}_{9.85}\text{O}_{35}:\text{Mn}_{0.15}, \text{Tm}_x$ ($x = 0.0, 0.2, 0.5, 0.6, 1.0$). Inset shows the Tm^{3+} concentration dependence of lattice parameter (a) and unit cell volume of the $\text{Ca}_{14-x}\text{Zn}_6\text{Al}_{9.85}\text{O}_{35}:\text{Mn}_{0.15}, \text{Tm}_x$ samples

Fig. 2. The SEM micrograph of the $\text{Ca}_{13.5}\text{Zn}_6\text{Al}_{9.85}\text{O}_{35}:\text{Mn}_{0.15},\text{Tm}_{0.5}$ sample.

Fig. 3. Excitation spectra of Mn^{4+} single doped sample monitored at 714 nm and $\text{Mn}^{4+}/\text{Tm}^{3+}$ co-doped sample monitored at 1.85 μm.

Fig. 4. Emission spectra of Mn^{4+} , Tm^{3+} single doped and $\text{Mn}^{4+}/\text{Tm}^{3+}$ co-doped phosphors with different concentrations of Tm^{3+} (a),(b)pumped by 455 nm and (c),(d) pumped by 360 nm. The inset shows the 714 nm, 800 nm, 1.47 μm and 1.85 μm emission intensity tendency when changing Tm^{3+} concentration ($x = 0.05, 0.1, 0.2, 0.5, 0.6$ and 1.0) and pump source.

Fig. 5. Emission spectra in range of 1600-2000nm for the Tm³⁺ single doped sample and the Mn⁴⁺-Tm³⁺ co-doped sample pumped by 455 nm light. The inset shows integral intensity of 1.85 μm emission band as a function of Mn⁴⁺ concentration (y = 0.0, 0.15, 0.3, 0.5, 0.6 and 1.0).

Fig. 6. Simplified energy level scheme and possible energy transfer mechanism between Mn^{4+} and Tm^{3+} ions.

Fig. 7. Decay curves of Mn⁴⁺ 714nm (a) and Tm³⁺ 800nm, 1.47μm, 1.85 μm emission (b), (c), (d) for Ca_{14-x}Zn₆Al_{9.85}O₃₅: 0.15Mn, xTm. The inset shows the energy transfer efficiency η_T from Mn⁴⁺ to Tm³⁺ dependence on the Tm³⁺ content.

Fig. 8. Dependence of τ_0/τ of Mn⁴⁺ on (a) $C^{6/3}$, (b) $C^{8/3}$, and (c) $C^{10/3}$.

References

- [1] Q. Wang, J. Geng, S. Jiang, 2- μm fiber laser sources for sensing, *Opt. Eng.* 53 (2014) 061609-061609.
- [2] F. Cornacchia, A. Toncelli, M. Tonelli, 2- μm lasers with fluoride crystals: Research and development, *Prog. Quant. Electron.* 33 (2009) 61-109.
- [3] P. Zhou, X. Wang, Y. Ma, et al., Review on recent progress on mid-infrared fiber lasers, *Laser Phys.* 22 (2012) 1744-1751.
- [4] B. Tunc, M. Gulsoy, Tm: Fiber laser ablation with real-time temperature monitoring for minimizing collateral thermal damage: ex vivo dosimetry for ovine brain, *Laser Surg. Med.* 45 (2013) 48-56.
- [5] M. Pollnau, S.D. Jackson, Mid-infrared fiber lasers [M]//Solid-State Mid-Infrared Laser Sources. Springer Berlin Heidelberg, 2003, pp. 225-261.
- [6] W.C. Wang, J. Yuan, D.D. Chen, et al., Enhanced 1.8 μm emission in $\text{Cr}^{3+}/\text{Tm}^{3+}$ co-doped fluorogermanate glasses for a multi-wavelength pumped near-infrared lasers, *AIP Adv.* 4 (2014) 107145-107145.
- [7] E.W. Duczynski, G. Huber, V.G. Ostroumov, et al., cw double cross pumping of the $^5\text{I}_7 - ^5\text{I}_8$ laser transition in Ho^{3+} -doped garnets, *Appl. Phys. Lett.* 48 (1986) 1562-1563.
- [8] U.R. Rodríguez-Mendoza, V.D. Rodríguez, I.R. Martín, et al., Cr^{3+} - Tm^{3+} energy transfer in alkali silicate, *Journal of alloys and compounds* 323 (2001) 759-762.
- [9] K. Li, Q. Zhang, G. Bai, et al., Energy transfer and 1.8 μm emission in $\text{Tm}^{3+}/\text{Yb}^{3+}$ codoped lanthanum tungsten tellurite glasses, *J. Alloy. Compd.* 504 (2010) 573-578.

- [10] J. Xie, Q. Zhang, Y. Zhuang, et al., Enhanced mid-IR emission in Yb^{3+} - Tm^{3+} co-doped oxyfluoride glass ceramics, *J. Alloy. Compd.* 509 (2011) 3032-3037.
- [11] F. Güell Vilà, J. Massons, J. Gavalda, et al., 1.84 micron emission of Tm^{3+} sensitized by Yb^{3+} ions in monoclinic $\text{KGd}(\text{WO}_4)_2$ single crystals, *J. Appl. Phys.* 101 (2007) 0331081-0331086.
- [12] S. Balaji, K. Biswas, A.D. Sontakke, et al., Enhanced 1.8 μm emission in $\text{Yb}^{3+}/\text{Tm}^{3+}$ co-doped tellurite glass: Effects of $\text{Yb}^{3+} \leftrightarrow \text{Tm}^{3+}$ energy transfer and back transfer, *J. Quant. Spectrosc. Ra.* 147 (2014) 112-120.
- [13] B. Richards, A. Jha, Y. Tsang, et al., Tellurite glass lasers operating close to 2 μm , *Laser Phys. Lett.* 7 (2010) 177-177.
- [14] F.E. Williams, Some new aspects of germanate and fluoride phosphors, *JOSA* 37 (1947) 302-307.
- [15] T.M. Chen, J.T. Luo, Highly saturated red-emitting Mn (IV) activated phosphors and method of fabricating the same: U.S. Patent 7,846,350[P]. 2010-12-7.
- [16] Y.X. Pan, G.K. Liu, Enhancement of phosphor efficiency via composition modification, *Opt. Lett.* 33 (2008) 1816-1818.
- [17] H.G. Kang, J.K. Park, C.H. Kim, et al., Luminescence properties of $\text{MAl}_{12}\text{O}_{19}$: Mn^{4+} (M= Ca, Sr, Ba) for UV LEDs, *J. Ceram. Soc. Jpn.* 117 (2009) 647-649.
- [18] P.A. Tanner, Z. Pan, Luminescence Properties of Lanthanide and Transition Metal Ion-Doped $\text{Ba}_2\text{LaNbO}_6$: Detection of MnO_6^{8-} and CrO_6^{9-} Clusters, *Inorg. Chem.* 48 (2009) 11142-11146.
- [19] S. Okamoto, H. Yamamoto, Luminescent-Efficiency Improvement by

- Alkaline-Earth Fluorides Partially Replacing MgO in $3.5 \text{ MgO} \cdot 0.5 \text{ MgF}_2 \cdot \text{GeO}_2$: Mn^{4+} Deep-Red Phosphors for Light Emitting Diodes, J. Electrochem. Soc. 157 (2010) J59-J63.
- [20] E.V. Radkov, A.A. Setlur, A.M. Srivastava, et al., Red line emitting phosphors for use in led applications: U.S. Patent 7,648,649[P]. 2010-1-19.
- [21] A.A. Setlur, E.V. Radkov, C.S. Henderson, et al., Energy-efficient, high-color-rendering LED lamps using oxyfluoride and fluoride phosphors, Chem. Mat. 22 (2010) 4076-4082.
- [22] M.G. Brik and A.M. Srivastava, On the optical properties of the Mn^{4+} ion in solids, J. Lumin. 133 (2013) 69-72.
- [23] M. Peng, X. Yin, P.A. Tanner, et al., Orderly-Layered Tetravalent Manganese-Doped Strontium Aluminate $\text{Sr}_4\text{Al}_{14}\text{O}_{25}:\text{Mn}^{4+}$: An Efficient Red Phosphor for Warm White Light Emitting Diodes, J. Am. Ceram. Soc. 96 (2013) 2870-2876.
- [24] T. Takahashi, S. Adachi, Synthesis of $\text{K}_2\text{SiF}_6:\text{Mn}^{4+}$ Red Phosphor from Silica Glasses by Wet Chemical Etching in HF/KMnO_4 Solution, Electrochem. Solid ST. 12 (2009) J69- J71.
- [25] S. Adachi, T. Takahashi, Photoluminescent properties of $\text{K}_2\text{GeF}_6:\text{Mn}^{4+}$ red phosphor synthesized from aqueous HF/KMnO_4 solution, J. Appl. Phys. 106 (2009) 3516.
- [26] T. Murata, T. Tanoue, M. Iwasaki, et al., Fluorescence properties of Mn^{4+} in $\text{CaAl}_{12}\text{O}_{19}$ compounds as red-emitting phosphor for white LED, J. Lumin. 114 (2005) 207-212.

- [27] K. Seki, K. Uematsu, T. Ishigaki, et al., Synthesis of Mn^{4+} doped red emitting phosphor for white LEDs, *J. Ceram. Process. Res.* 12 (2011) S286- S288.
- [28] B. Wang, H. Lin, J. Xu, et al., $\text{CaMg}_2\text{Al}_{16}\text{O}_{27}$: Mn^{4+} -based Red Phosphor: A Potential Color Converter for High-Powered Warm W-LED, *ACS Appl. Mater. Interfaces* 6 (2014) 22905-22913.
- [29] W. Lü, W. Lv, Q. Zhao, et al., A Novel Efficient Mn^{4+} Activated $\text{Ca}_{14}\text{Al}_{10}\text{Zn}_6\text{O}_{35}$ Phosphor: Application in Red-Emitting and White LEDs, *Inorg. Chem.* 53 (2014) 11985-11990.
- [30] K. Seki, K. Uematsu, K. Toda, et al., Novel Deep Red Emitting Phosphors $\text{Ca}_{14}\text{Zn}_6\text{M}_{10}\text{O}_{35}$: Mn^{4+} ($\text{M} = \text{Al}^{3+}$ and Ga^{3+}), *Chem. Lett.* 43 (2014) 1213-1215.
- [31] M. Aoyama, Y. Amano, K. Inoue, et al., Synthesis and characterization of Mn-activated lithium aluminate red phosphors, *J. Lumin.* 136 (2013) 411-414.
- [32] J. Lü, Y. Huang, Y. Tao, et al., Spectroscopic parameters of Ce^{3+} ion doped $\text{Na}_2\text{CaMg}(\text{PO}_4)_2$ phosphor, *J. Alloys Compd.* 500 (2010) 134-137.
- [33] J. Zhou, Y. Teng, X. Liu, et al., Intense infrared emission of Er^{3+} in $\text{Ca}_8\text{Mg}(\text{SiO}_4)_4\text{Cl}_2$ phosphor from energy transfer of Eu^{2+} by broadband down-conversion. *Opt. Express* 18(2010) 21663-21668.
- [34] J. Meuldijk, R. van der Meulen, H.W. Den Hartog, Dielectric-relaxation experiments on cubic solid solutions of SrF_2 and CeF_3 or PrF_3 , *Phys. Rev. B* 29 (1984) 2153.
- [35] D. Chen, L. Lei, J. Xu, et al., Abnormal size-dependent upconversion emissions and multi-color tuning in Er^{3+} -doped $\text{CaF}_2\text{--YbF}_3$ disordered solid-solution

nanocrystals, Nanotechnology 24 (2013) 085708.

[36] H. Jing, C. Guo, G. Zhang, et al., Photoluminescent properties of Ce^{3+} in compounds $\text{Ba}_2\text{Ln}(\text{BO}_3)_2\text{Cl}$ ($\text{Ln} = \text{Gd}$ and Y), J. Mater. Chem. 22 (2012) 13612-13618.

[37] P.I. Paulose, G. Jose, V. Thomas, et al., Sensitized fluorescence of $\text{Ce}^{3+}/\text{Mn}^{2+}$ system in phosphate glass, J. Phys. and Chem. Solids 64 (2003) 841-846.

[38] B.M. ANTIPENK, I.M. Bataev, V.L. Ermolaev, et al., Ion-to-ion radiationless transfer of electron excitation energy between rare-earth ions in $\text{POCl}_3\text{-SnCl}_4$, Opt. Spectrosc.-USSR 29 (1970) 177.

[39] G. Blasse, Energy transfer in oxidic phosphors, Philips Res. Rep 24 (1969), 131-44.

[40] R. Reisfeld, E. Greenberg, R. Velapoldi, et al., Luminescence quantum efficiency of Gd and Tb in borate glasses and the mechanism of energy transfer between them, J. Chem. Phys. 56 (1972) 1698-1705.

[41] D.L. Dexter, J.H. Schulman, Theory of concentration quenching in inorganic phosphors, J. Chem. Phys. 22 (1954) 1063-1070.