

Efficient green emission by up-conversion in Yb³⁺/Er³⁺ co-doped monoclinic AgGdW₂O₈

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Yb³⁺/Er³⁺ co-doped monoclinic AgGdW₂O₈ phosphors with intense green emission via up-conversion process were prepared by the high-temperature solid-state method. The samples were structurally characterized using X-ray powder diffraction, after which their luminescent properties were characterized via up-conversion spectroscopy. Green and red emissions centered at 525, 550, and 656 nm were observed when the phosphors were excited at 980 nm, these emissions are ascribed to ²H_{11/2}, ⁴S_{3/2} → ⁴I_{15/2} (green emission) and ⁴F_{9/2} → ⁴I_{15/2} (red emission) transitions of Er³⁺, respectively. It was also found that the green and red emissions originated from the two-photon process. By increasing sintering temperature and doping of Mo⁶⁺, the structure of monoclinic AgGdW₂O₈ transformed to a tetragonal one, which resulted a dramatic increase in UC intensity.

Key words: AgGd(W, Mo)₂O₈ : Yb,Er, Up-conversion, Monoclinic.

Introduction

Over the past several decades, up-conversion (UC) materials, which are used to convert infrared radiation to visible wavelengths, have attracted considerable interest due to their potential applications in bio-imaging, solar cells, sensors and so on [1, 2]. For UC luminescence, the present efficiency cannot satisfy the ever growing needing, and which inspired people to search new material continuously.

Many Rare Earth (RE) ions played key role in UC materials. Er³⁺ was suitable for the activator ion for infrared to visible light. Yb³⁺ was an ideal sensitizer ion. Therefore, Yb³⁺/Er³⁺ were often chose as doped ions in UC materials. Among oxide host materials, phonon cutoff frequency of MRe(XO₄)₂ was relatively low, which was found to be helpful to increase its UC intensity. In addition, strong polarization, which caused by larger electric charge and small radius of X⁶⁺ in MRe(XO₄)₂ (M = Li, Na, K, and Ba; X = W and Mo) matrix, would decrease symmetries, and enhance energy splitting of Er³⁺ in the crystal field [3]. AgGdW₂O₈ would take two different structures depending on synthesized conditions. The monoclinic phase can be obtained below 850 °C, named as low temperature phase (LP) and the tetragonal phase obtained at temperature higher than 1000 °C, named as high temperature phase (HP). Recently, the structure and luminescence properties of rare earth (RE)-doped tetragonal-phase AgGdW₂O₈ [4-5] have been studied in detail. In our early work, green UC luminescence of Er³⁺/Yb³⁺ co-

doped tetragonal-phase AgGdW₂O₈ phosphors was synthesized and investigated in detail [6]. However, to the best of our knowledge, the UC properties of monoclinic phase AgGdW₂O₈ have not yet been reported. In this work, Er³⁺/Yb³⁺ co-doped monoclinic AgGdW₂O₈ phosphors were synthesized via the solid-state method. The structure and UC properties of the samples were investigated.

Experimental

The AgGd_{1.000-δ-x}Yb_δEr_x(W_{1.000-y}Mo_yO₄)₂ (δ = 0.100-0.500, x = 0.005-0.035, y = 0.000-1.000) molecular formula is used to express the different compositions of the synthesized samples. The samples were synthesized using the traditional high-temperature solid-state reaction. The starting materials were Ag₂O (A.R.), WO₃ (A.R.), MoO₃ (A.R.), Gd₂O₃ (99.99%), Yb₂O₃ (99.99%), and Er₂O₃ (99.99%). First, Gd₂O₃, Yb₂O₃, and Er₂O₃ were separately calcined at 1073 K for 2 h. Then, the raw material was weighed according to the stoichiometric ratio. The materials were mixed thoroughly in an agate mortar and sintered at 1073 K for 4 h in air.

The structures of the synthesized samples were identified using a Rigaku D/Max-3C X-ray powder diffractometer. The UC spectra were measured with a Hitachi F-4600 fluorescence spectrophotometer with a 980 nm semiconductor laser as the excitation source.

Results and Discussion

Structures of AgGd(WO₄)₂ with different doping concentration of Yb³⁺

Fig. 1 shows the X-ray diffraction (XRD) patterns of AgGd(WO₄)₂ with different doping concentration of

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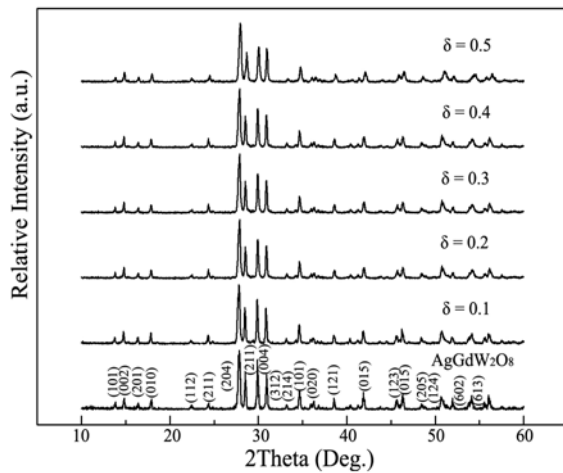


Fig. 1. XRD patterns of $\text{Ag}(\text{Gd}_{1.000-\delta}\text{Yb}_{\delta})(\text{WO}_4)_2$ ($0.100 \leq \delta \leq 0.500$).

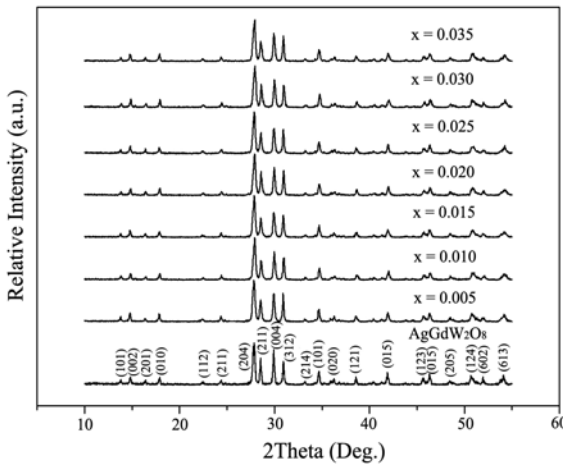


Fig. 2. XRD patterns of $\text{AgGd}_{0.800-x}\text{Yb}_{0.200}\text{Er}_x(\text{WO}_4)_2$ ($x = 0.005-0.035$).

Yb^{3+} . For there was no standard diffraction card of AgGdW_2O_8 , our results were compared with ref [4]. It was found that the structures of AgGdW_2O_8 with different doping concentration of Yb^{3+} are all monoclinic. Also according to our early experiments and references [7, 8], the optimal Yb^{3+} concentration is set as 20 mol%.

Structures and luminescence properties of $\text{AgGd}_{0.800-x}\text{Yb}_{0.200}\text{Er}_x(\text{WO}_4)_2$ ($x = 0.005-0.035$)

The structures of $\text{AgGd}_{0.800-x}\text{Yb}_{0.200}\text{Er}_x(\text{WO}_4)_2$ ($x = 0.005-0.035$) were characterized; their XRD patterns are exhibited in Fig. 2. Structure study illustrated that AgGdW_2O_8 belongs to the scheelite structure, with a monoclinic unit cell: $a = 1.0775$ nm, $b = 0.4987$ nm, $c = 1.3005$ nm and $\beta = 114.00^\circ$ [4]. As shown, it was found that the positions of the diffraction lines with different Er^{3+} contents were similar to that of monoclinic AgGdW_2O_8 , it also demonstrated that doping with Yb^{3+} and Er^{3+} did not cause structural changes to AgGdW_2O_8 .

The detailed UC properties of these samples were fully investigated. They all produced UC emission in

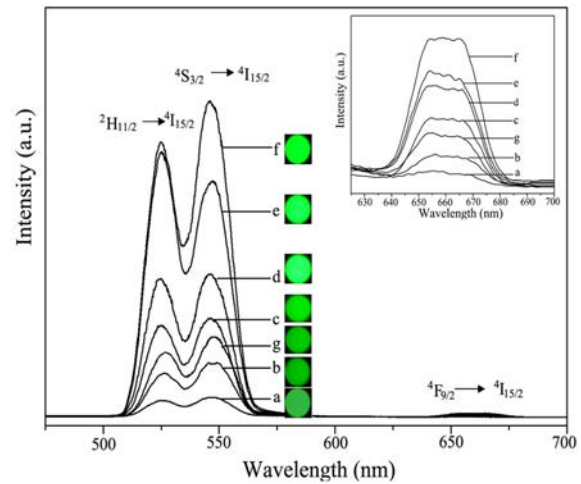


Fig. 3. UC spectra of $\text{AgGd}_{0.800-x}\text{Yb}_{0.200}\text{Er}_x(\text{WO}_4)_2$ ($x = 0.005-0.035$). (a) 0.005, (b) 0.010, (c) 0.015, (d) 0.020, (e) 0.025, (f) 0.030, (g) 0.035.

the visible region when excited by a 980 nm semiconductor laser (Fig. 3). The UC spectra of $\text{AgGd}_{0.800-x}\text{Yb}_{0.200}\text{Er}_x(\text{WO}_4)_2$ ($x = 0.005-0.035$) are composed of two parts in the ranges of 500-580 nm and 630-690 nm, which correspond to green and red emissions, respectively. The emission in the range of 500-580 nm is composed of two peaks that are centered at 525 and 550 nm; these peaks are ascribed to the transitions of Er^{3+} ($^2\text{H}_{11/2}$, $^4\text{S}_{3/2} \rightarrow ^4\text{I}_{15/2}$). The weaker emission in the range of 630-690 nm is due to the $^4\text{F}_{9/2} \rightarrow ^4\text{I}_{15/2}$ transition of Er^{3+} . Since the emission in the range of 630-690 nm is relatively weak, the color of the samples, as observed by human eyes, is green. With increasing of Er^{3+} concentration, the UC emission intensity increased, maximized at 3 mol% Er^{3+} concentrations, and then decreased. The optimum Er^{3+} concentration should be 3 mol%.

Structures and luminescence properties of $\text{AgGd}_{0.770}\text{Yb}_{0.200}\text{Er}_{0.030}(\text{W}_{1.000-y}\text{Mo}_y\text{O}_4)_2$ ($y = 0.000-1.000$)

It has been widely reported that it is possible to enhance PL intensity using a solid solution of tungstate and molybdate [4, 9]. However, there are few reports regarding them in UC luminescent materials. In this work, we tried to explore the influences of Mo^{6+} doped on $\text{AgGd}_{0.770}\text{Yb}_{0.200}\text{Er}_{0.030}(\text{WO}_4)_2$ structure and UC luminescent properties. The XRD patterns of $\text{AgGd}_{0.770}\text{Yb}_{0.200}\text{Er}_{0.030}(\text{W}_{1.000-y}\text{Mo}_y\text{O}_4)_2$ ($y = 0.000-1.000$) samples which were sintered at 1073 K for 4 h were shown in Fig. 4. When the doped concentration of Mo^{6+} increased, the system undergone a composition induced phase transition from monoclinic to tetragonal structure. When the doped concentration of Mo^{6+} was greater than 40 mol%, the diffraction peaks matched well with the standard diffraction card (JCPDS 53-0042) of pure tetragonal $\text{AgGdMo}_2\text{O}_8$ (tetragonal, $a = b = 5.2220$ Å, $c = 11.4758$ Å, space group $I41/\alpha$).

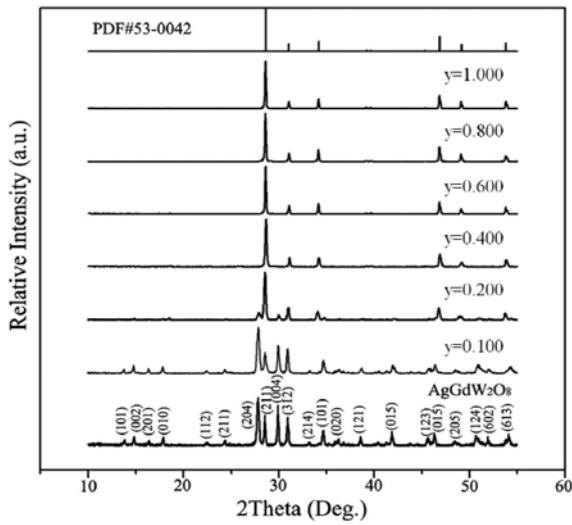


Fig. 4. XRD patterns of $\text{AgGd}_{0.770}\text{Yb}_{0.200}\text{Er}_{0.030}(\text{W}_{1.000-y}\text{Mo}_y\text{O}_4)_2$ ($y = 0.000-1.000$).

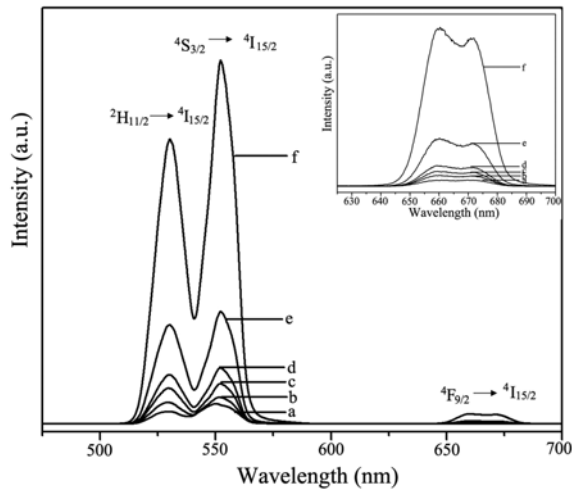


Fig. 5. UC spectra of $\text{AgGd}_{0.770}\text{Yb}_{0.200}\text{Er}_{0.030}(\text{W}_{1.000-y}\text{Mo}_y\text{O}_4)_2$ ($y = 0.000-1.000$). (a) $y = 0.000$, (b) $y = 0.100$, (c) $y = 0.200$, (d) $y = 0.400$, (e) $y = 0.600$, (f) $y = 1.000$.

The effect of the doping concentration of Mo^{6+} contribution on the UC luminescent spectra of $\text{AgGd}_{0.770}\text{Yb}_{0.200}\text{Er}_{0.030}(\text{WO}_4)_2$ was also studied in detail. Fig. 5 shows the UC luminescence spectra of $\text{AgGd}_{0.770}\text{Yb}_{0.200}\text{Er}_{0.030}(\text{W}_{1-y}\text{Mo}_y\text{O}_4)_2$ ($y = 0.000-1.000$). As seen from spectra, the position and profile of peaks were analogous to that of Fig. 3, whereas the intensities of emission peaks were altered with the varied concentration of Mo^{6+} . The intensity of emission was increased with the rising of Mo^{6+} concentration. When Mo^{6+} concentration increased to 100 mol%, the UC luminescence intensity reached its maximum and became more than 17.3 times to that of the Mo^{6+} undoped sample.

In our early work [6], the UC intensity of HP- $\text{AgGd}_{0.775}\text{Yb}_{0.200}\text{Er}_{0.025}(\text{MoO}_4)_2$ was the highest followed by that of $\text{AgGd}_{0.775}\text{Yb}_{0.200}\text{Er}_{0.025}(\text{WO}_4)_2$. Based on our early experiment results, the UC luminescence spectra of

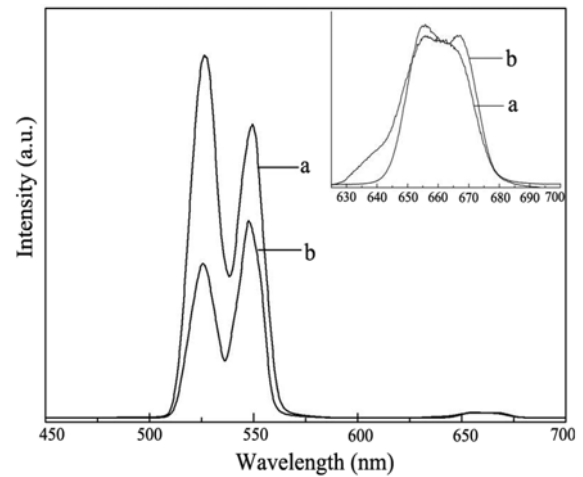


Fig. 6. UC spectra of $\text{AgGd}_{0.775}\text{Yb}_{0.200}\text{Er}_{0.025}(\text{MoO}_4)_2$ prepared at (a) 1373 K and (b) 1073 K (Inset: Enlarged spectra in the red emission region).

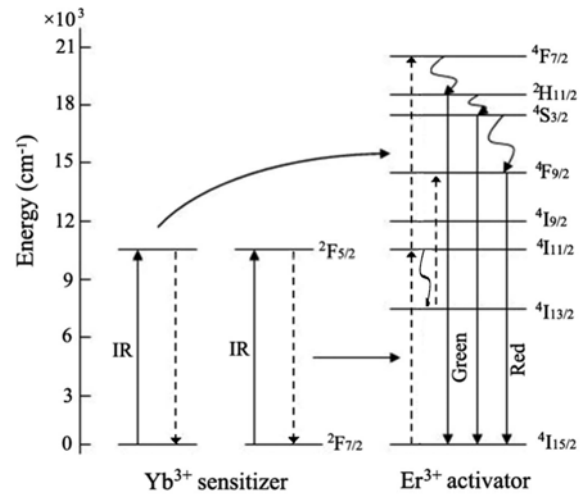


Fig. 7. Energy level diagrams of Yb^{3+} and Er^{3+} in AgGdW_2O_8 and the luminescent process.

the different preparation temperature $\text{AgGdMo}_2\text{O}_8 : \text{Yb,Er}$ are shown in Fig. 6. As seen, the green UC emission intensity of $\text{AgGdMo}_2\text{O}_8 : \text{Yb,Er}$ prepared at 1373 K was significantly 2 times higher than that of $\text{AgGdMo}_2\text{O}_8 : \text{Yb,Er}$ prepared at 1073 K, but the red UC emission intensity was similar. Also the green UC emission intensity that centered at 525 and 550 nm show a slightly difference different, this might be related to the different preparation temperatures.

A schematic energy level diagram and visible emission processes for the $\text{Yb}^{3+}/\text{Er}^{3+}$ systems were shown in Fig. 7. Upon excitation of the samples with the 980 nm semiconductor laser, Yb^{3+} ions are excited from the $^2\text{F}_{7/2}$ ground state to the $^2\text{F}_{5/2}$ excited state. Through an efficient sequential energy-transfer process from two excited Yb^{3+} ions to the ground state of the Er^{3+} ions, resulting in a population of Er^{3+} from $^4\text{I}_{15/2}$ to $^4\text{I}_{11/2}$, then part of the electrons in the $^4\text{I}_{11/2}$ level non-radiatively relax to the lower $^4\text{I}_{13/2}$. Then a second 980

nm photon transferred by the excited Yb^{3+} ion can then populate a higher $^4\text{F}_{9/2}$ energetic state of the Er^{3+} ion, and produce red emissions centered at 656 nm with a transition to ground state. Also, the second 980 nm photon transferred by the excited Yb^{3+} ion can then populate a higher $^4\text{F}_{7/2}$ energetic state of the Er^{3+} ion. Then, the electrons in the $^4\text{F}_{7/2}$ level non-radiatively relax to the lower $^2\text{H}_{11/2}$, $^4\text{S}_{3/2}$, and $^4\text{F}_{9/2}$ levels to produce three emissions centered at 525, 550, and 656 nm, respectively, upon the radiative transition to the $^4\text{I}_{15/2}$ ground state. The cross relaxation efficiency was very low, because the energy gaps among the $^2\text{H}_{11/2}$, $^4\text{S}_{3/2}$, and $^4\text{F}_{9/2}$ were very small, which caused the depopulation of the $^4\text{F}_{7/2}$ level, and result of in a weak red emission.

Conclusions

A new UC material, $\text{Yb}^{3+}/\text{Er}^{3+}$ co-doped monoclinic AgGdW_2O_8 were synthesized by the traditional high-temperature solid-state method and then structurally and spectroscopically characterized. The results indicated that the UC intensity of the monoclinic $\text{AgGd}_{0.800-x}\text{Yb}_{0.200}\text{Er}_x(\text{WO}_4)_2$ ($x = 0.005-0.035$) was dependent on the doping concentration of Er^{3+} , an optimal doping concentration of 3 mol% Er^{3+} in the AgGdW_2O_8 host was established. By doping of Mo^{6+} , the structure

of AgGdW_2O_8 transformed to a tetragonal one, which resulting a dramatic increasing in UC intensity. $\text{AgGd}_{0.770}\text{Yb}_{0.200}\text{Er}_{0.030}(\text{MoO}_4)_2$ exhibited an intense UC emission, which was about 17.3 times to that of the LP- $\text{AgGd}_{0.770}\text{Yb}_{0.200}\text{Er}_{0.030}(\text{WO}_4)_2$. In addition, the UC intensity of $\text{AgGdMo}_2\text{O}_8 : \text{Yb,Er}$ prepared at 1073 K was weaker than that of $\text{AgGdMo}_2\text{O}_8 : \text{Yb,Er}$ prepared at 1373 K, and the possible reason is proposed.

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