Quasi-one dimensional Er\(^{3+}\)–Yb\(^{3+}\) codoped single-crystal MoO\(_3\) ribbons: Synthesis, characterization and up-conversion luminescence

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Abstract

The quasi-one dimensional (Q1D) Er\(^{3+}\)–Yb\(^{3+}\) codoped single-crystal MoO\(_3\) ribbons with width range from 1 to 5 μm, and maximum length about 30 μm have been synthesized by the vapor transport method. The samples were characterized using X-ray diffraction, scanning electron microscopy, transmission electron microscope, and luminescence spectra. By a 975 nm laser diode (LD) as excitation source, the blue, green and red emission bands centered at about 408, 532, 553 and 657 nm were detected, which attributed to the \(^{2}H_{9/2}\)→\(^{4}I_{15/2}\), \(^{2}H_{11/2}\)→\(^{4}I_{15/2}\) and \(^{4}F_{9/2}\)→\(^{4}I_{15/2}\) transitions of Er\(^{3+}\), respectively. The three- and two-photon process was responsible for the blue, green and red up-conversion emissions mechanism for the Q1D Er\(^{3+}\)–Yb\(^{3+}\) codoped single-crystal MoO\(_3\) ribbons, respectively. The results suggested that the Q1D Er\(^{3+}\)–Yb\(^{3+}\) codoped single-crystal MoO\(_3\) ribbons will have potential applications in remote bio-imaging and surface enhanced Raman scattering.

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1. Introduction

There has been a great interest in applying rare-earth ions doped up-conversion emissions materials in the fields of color display, near infrared detectors, biological diagnosis, laser cooling and temperature sensor [1–6]. Among the rare-earth ions, Er\(^{3+}\) is one of the most popular and efficient ions due to its visible up-conversion and infrared emissions using a 975 nm semiconductor laser diodes (LD) as excitation source [1,2]. However, the relatively low absorption cross-section of about 1.7×10\(^{−21}\) cm\(^2\) made the ground state absorption (GSA) of Er\(^{3+}\) at 975 nm very weak, leading to reduction of the emission intensity and the pump efficiency. It is well known that Yb\(^{3+}\) with a large absorption cross section at near infrared (NIR) can act as a photo-sensitizer to overcome the difficulty associated with the rather small absorption cross section of Er\(^{3+}\) due to the dipole-forbidden nature of intra-\(4f\) transitions [7,8]. The NIR photon energy is transferred efficiently from Yb\(^{3+}\) to Er\(^{3+}\), and the up-conversion occurs when the subsequent energy transfer (ET) process promote electrons of Er\(^{3+}\) to high-lying energy levels whose radiative decay leads to up-conversion emission [9,10].

Up to date, stronger up-conversion emissions were achieved for the Er\(^{3+}\) doped sulfide-, chloride-, and fluoride-based materials because of their low phonon energies [11]. Compared with these materials above, rare-earth ions doped oxides have higher chemical durability, thermal stability, and mechanical strength, which will have wider practical application in the future [12].

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Fig. 1. The XRD pattern of Er\(^{3+}\)–Yb\(^{3+}\) codoped MoO\(_3\) Q1D ribbons.

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attracting an increasing interest for both fundamental and applied science.

In the recent years, there are extensive researches about rare-earth doped oxides, which mainly include ZnO, ZrO2, TiO2, Y2O3, Al2O3, Lu2O3 nanocrystals, and etc. [15–20]. However, there is little study about Q1D rare-earth ions doped oxides. Among transition-metal oxides, MoO3 has many distinctive properties and was used in field-emission, gas sensors, and et al. [21,22]. Also, MoO3 can be develop Q1D objects, and the Q1D MoO3 ribbons as substrate has been successfully applied to study of local and remote chemical enhanced on surface enhanced Raman scattering [23,24].

In this paper, we presented the experimental results about phase structure, morphology, blue, green and red up-conversion emissions of the Er3+–Yb3+ codoped MoO3 Q1D ribbons synthesized by a vapor transport method, in order to explore the Q1D rare-earth doped up-conversion emission oxides materials and corresponding up-conversion mechanisms.

2. Experimental section

2.1. Synthesis

The Q1D Er3+–Yb3+ codoped single-crystal MoO3 ribbons have been synthesized by the vapor transport method. Er(NO3)3·5H2O (0.2 g), Yb(NO3)3·5H2O (1.8 g), and (NH4)6Mo7O24·4H2O (10 g) were placed in an Al2O3 crucible and heated to the sintering temperature of 1523 K with a heating rate of 5 K min⁻¹, maintained for 1 h. The gap between the door and the furnace was enlarged to have a 3–4 mm free space for easy airflow, and the Q1D Er3+–Yb3+ codoped single-crystal

Fig. 2. The SEM and TEM images of Er3+–Yb3+ codoped MoO3 Q1D ribbons.
MoO₃ ribbons with white color and transparent grow in a certain region with 600–800 K near the door of the furnace.

2.3. Results and discussion

3. Characterization

3.1. Characterization

Fig. 1 shows the XRD pattern of the Q1D Er³⁺–Yb³⁺ codoped single-crystal MoO₃ ribbons, which indicate that the ribbons consist of α-MoO₃ phase. The diffraction peaks of the XRD pattern for Er³⁺–Yb³⁺ codoped MoO₃ Q1D ribbons can be readily indexed to be orthorhombic with lattice constants of a = 3.962 Å, b = 13.855 Å, c = 3.701 Å (JCPDS no. 89-5108). Observation of only (0 1 0) lines in the diffraction pattern of the as-grown ribbons shows that the thickness of the ribbons is along the b-axis, which indicated the good crystal orientation and crystal quality of Er³⁺–Yb³⁺ codoped MoO₃ Q1D ribbons. The diffraction pattern of the as-grown ribbons shows that the thickness of the ribbons is along the b-axis, which indicated the good crystal orientation and crystal quality of Er³⁺–Yb³⁺ codoped MoO₃ Q1D ribbons.

Fig. 2(a)–(d) show the morphology investigations with characterized by SEM. The width range of the MoO₃ ribbons is about from 1 to 5 μm, and maximum length is about 30 μm. Surface of the Q1D Er³⁺–Yb³⁺ codoped single-crystal MoO₃ ribbons is clean, flat, and has no obvious defects. To further examine the microstructure features of the as-prepared MoO₃ sample, we carried out TEM measurements. Fig. 2(e) presents one of the typically observed rectangular shape of MoO₃ crystals, along with its corresponding electron diffraction pattern as an inset. From the indices of the electron pattern and the sharp diffraction spots, one can conclude the good crystal orientation and crystal quality of Er³⁺–Yb³⁺ codoped MoO₃ Q1D ribbons.

Fig. 3 shows the room-temperature visible up-conversion emission spectrum centered at about 408 nm, and 2 for the green up-conversion emission centered at about 532 nm, and 2 for the green up-conversion emission centered at about 532 nm, 553 nm, and 657 nm, respectively. The possible up-conversion emissions mechanism can be deduced on the basis of energy matching conditions. The logarithmic dependence of peak intensity of the blue, green and red up-conversion emissions were examined and the results for 408, 532, 553 and 657 nm are depicted in the log–log plot as shown as Fig. 4.

The dependence of the blue, green and red up-conversion emissions intensity upon the pump power was examined and the results for 408, 532, 553 and 657 nm are depicted in the log–log plot as shown as Fig. 4. The up-conversion emission intensity (Iup) is proportional to the n-th power of the pump power (Ppump) [25], as

\[ I_{up} \propto P_{pump}^n \quad (1) \]

where n is the number of photon0073 required to populate the blue, green and red up-conversion emissions states. The experimental data of up-conversion emission intensity were fitting to straight lines with a slope of n. The value of n is approximately equal to 3 for the blue up-conversion emission centered at about 408 nm, and 2 for the green and red up-conversion emissions centered at about 532, 553, and 657 nm, indicating that the three-, and two-photon process was responsible for the blue, green and red up-conversion emissions mechanism for the Q1D Er³⁺–Yb³⁺ codoped single-crystal MoO₃ ribbons, respectively.

The possible up-conversion emissions mechanism can be deduced on the basis of energy matching conditions. Fig. 5 shows the energy level diagram of the blue, green and red up-conversion emissions for the Q1D Er³⁺–Yb³⁺ codoped single-crystal MoO₃ ribbons by a 975 nm LD excitation. When using a 975 nm LD as excitation source, Er³⁺ at ground state (4I_{15/2}) was excited to the 4I_{11/2} level, followed by...
the ET (I) of $2F_{5/2}(Yb^{3+}) + 4I_{11/2}(Er^{3+}) \rightarrow 2F_{7/2}(Yb^{3+}) + 4I_{15/2}(Er^{3+})$ process. The red up-conversion emission was produced by the transition of $F_{4d} \rightarrow 4I_{15/2}$, the population of $F_{4d}$ level was ascribed to the non-radiative relaxation of $S_{5/2} \rightarrow 4F_{9/2}$. ET (II) of $2F_{5/2}(Yb^{3+}) + 4I_{11/2}(Er^{3+}) \rightarrow 2F_{7/2}(Yb^{3+}) + 4F_{9/2}(Er^{3+})$ processes. For the green up-conversion emissions, the ET (III) of $F_{5/2}(Yb^{3+}) + 4I_{11/2}(Er^{3+}) \rightarrow 2F_{7/2}(Yb^{3+}) + 4F_{9/2}(Er^{3+})$. The blue up-conversion emissions was attributed to the transition of $F_{5/2}(Yb^{3+}) + 4F_{9/2}(Er^{3+}) \rightarrow 2F_{7/2}(Yb^{3+}) + 2H_{9/2}(Er^{3+})$ process.

4. Conclusions

In summary, the Q1D Er$^{3+}$-Yb$^{3+}$ codoped single-crystal MoO$_3$ ribbons with width range from 1 to 5 μm, and maximum length about 30 μm have been synthesized by a vapor transport method. The resultant samples were characterized using XRD, SEM, TEM and up-conversion emissions spectra. The Er$^{3+}$-Yb$^{3+}$ codoped MoO$_3$ Q1D ribbons are α phase, orthorhombic with lattice constants of $a=3.962$ Å, $b=13.855$ Å, $c=3.701$ Å, and the thickness of the ribbons is along the b-axis. The blue, green and red emission bands centered at about 408, 532, 553 and 657 nm were detected, which attributed to the $2H_{9/2} \rightarrow 4I_{15/2}, 2H_{11/2}, 5S_{3/2} \rightarrow 4I_{15/2}$ and $4F_{5/2} \rightarrow 4I_{15/2}$ transitions of Er$^{3+}$, respectively. The three- and two-photon process was responsible for the blue, green and red up-conversion emissions mechanism for the Q1D Er$^{3+}$-Yb$^{3+}$ codoped single-crystal MoO$_3$ ribbons, respectively.

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References


Fig. 5. The energy level diagram of the blue, green and red up-conversion emissions from Er$^{3+}$-Yb$^{3+}$ codoped MoO$_3$ Q1D ribbons by a 975 nm LD excitation.

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