Fluorescence properties of divalent and trivalent europium ions in $CdWO_4$ single crystals grown by the Bridgman method*

Hu Hao-Yang(胡皓阳)[a], Xia Hai-Ping(夏海平)[a]†, Hu Jian-Xu(胡建旭)[a], Zhang Yue-Pin(张约品)[a], Jiang Hao-Chuan(江浩川)[b], and Chen Hong-Bing(陈红兵)[c]

[a] *Key Laboratory of Photo-electronic Materials, Ningbo University, Ningbo* 315211, *China*
[b] *Ningbo Institute of Materials Technology and Engineering, the Chinese Academy of Sciences, Ningbo* 315211, *China*
[c] *Faculty of Material Science and Chemical Engineering, Ningbo University, Ningbo* 315211, *China*

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Optical absorption, excitation, and fluorescence were investigated in Eu ion-doped $CdWO_4$ single crystal grown by a modified Bridgman method. The results indicate that Eu^{2+} and Eu^{3+} ions coexist in $CdWO_4$ crystal and an energy transfer occurs between these Eu^{2+} and Eu^{3+} ions. When the crystal is excited by 266-nm light, the energy corresponding to the $4f^65d$ to $^8S_{7/2}$ transition of Eu^{2+} ions results in the excitation of the Eu^{3+} ions to the ^5D_J level. The effect on fluorescence of annealing in oxygen at various temperatures was investigated. The excitation intensity of Eu^{2+} ions at 266 nm decreases as annealing temperature increases from 300 K to 1073 K, but it remains at a certain equilibrium level when the annealing temperature is further increased.

Keywords: Eu^{2+} ion, optical spectra, cadmium tungstate, Bridgman method

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1. Introduction

Crystals containing Eu^{2+} ions have been extensively studied because of their large potential for applications in optical fields such as phosphors, electroluminescent materials, scintillators, and high-density optical storage.[1] Generally speaking, Eu ions can exist in both divalent and trivalent states, but they tend to stay trivalent. Techniques have been used to obtain crystals containing a larger proportion of divalent Eu ions. For instance, crystals were grown in a reduced atmosphere. In addition to their fabrication conditions and treatment atmosphere, it has been demonstrated that the composition and structure of the matrix plays a very important role in the valence state of Eu ions and related optical properties. We note that some Eu^{2+} ions exist in some borate,[2–5] silicate,[6–8] and tellurate[9] compositions although they are fabricated in an air atmosphere.

Cadmium tungstate ($CdWO_4$) is important for its applications in scintillators and other optical devices[10] because of its good thermal stability, low radiation damage, high average refractive index, and high X-ray absorption coefficient.[11] In recent years, $CdWO_4$ doped with rare earth ions has been widely studied because it is a candidate host material for promising applications in phosphors.[12,13] To our knowledge, although the growth and optical characteristics of metal tungstate crystals doped with rare earth ions have been widely reported,[14,15] there are few studies focusing on the europium ion-doped $CdWO_4$ crystals. In this paper, our results related to the growth of the europium ion-doped $CdWO_4$ crystals by a modified Bridgman method are reported. It is interesting that Eu^{2+} and Eu^{3+} ions co-exist in the as-grown $CdWO_4$ crystal even when the crystal was neither grown in a reduced atmosphere nor post-treated in such an atmosphere. To further understand how the post processing can affect the divalent and trivalent equilibrium of Eu ions as well as the effects on the optical characteristics of the crystal, we studied the annealing process at various temperatures.

2. Experiment

$CdWO_4$ single crystals were grown using the Czochralski (CZ) technique in previous work.[16] Generally speaking, it is difficult to obtain big $CdWO_4$ single crystals in this way due to the continuous composition change of the melt, which results from the different volatilization of CdO and WO_3 in the growing process, and cracking readily occurs in the as-grown crystals due to cleavage. In our process, a modified Bridgman process was applied to grow Eu-doped $CdWO_4$ crystal, in which harmful volatilization was minimized by sealing the crucibles, and the cracking of the crystals was reduced under favorable technical conditions.

The feed material for the europium-doped $CdWO_4$ crystal was synthesized from a mixture of high purity CdO (99.99 wt%), WO_3 (99.99 wt%), and Eu_2O_3 (99.99 wt%) at a

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†Corresponding author. E-mail: xiahaiping@nbu.edu.cn

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molar ratio of 1:1:0.005. The mixtures were ground for 1 hour in a mortar and sintered at 1150 °C for 6 hours in a furnace, yielding light red polycrystals through a solid state reaction. The doping concentration for a single crystal was 0.5 mol%.

The single crystal was grown by a two-zone resistivity heated vertical Bridgman furnace. The temperature of the furnace was adjusted with an accuracy of ±0.5 °C by a temperature controller. The temperature of the melting zone was usually controlled at 1355 °C, 100 °C higher than the melting point of the crystal. The platinum crucible used in crystal growth was about 25 mm in diameter and 120 mm–180 mm in length with a seed well of 10 mm in diameter at the bottom of the cylinder. Pt–Pt/Rh 10% thermocouples were used to detect the temperatures along the crucible. The mixtures were put into the Pt crucible with cylinder shape and a seed of the $CdWO_4$ single crystal with the *c*-axis direction was placed at the bottom. The crucible was sealed and then put into the furnace chamber for crystal growth. No reducing agents were used in the process.

In a typical run, the furnace chamber was gradually heated to 1355 °C and maintained at that temperature. The crucible was then adjusted to a position where only the top of the seed was melted. The feed materials and the top of the seed were kept in a molten state for 5 hours, after which the crucible was pulled down at approximately 0.5 mm/h. The temperature gradient across the solid–liquid interface was from 50 °C/cm to 60 °C/cm, because this temperature gradient is beneficial for achieving higher quality crystals. The growth process was similar to that of $CdWO_4$ crystal demonstrated in detail in Ref. [17], and a schematic of the apparatus used for the modified Bridgman method is also shown in Ref. [18].

The as-grown crystals were cut into small pieces, and well polished to ∼2.5 mm thickness. These samples were used for investigating the luminescence properties. The annealing process was conducted at various temperatures in oxygen atmosphere, and crystals were held at the annealing temperature for 24 hours, and then cooled to 298 K at 100 °C/h.

The absorption spectra were measured with a Perkin–Elmer Lambda 950 Spectrophotometer and the excitation and fluorescence spectra were recorded on an F-4500 Spectrophotometer. All the measurements were carried out at 298 K.

3. Results and discussion

3.1. The existence of Eu^{2+} and Eu^{3+} ions in the crystal

Figure 1 shows a photo of the as-grown Eu-doped $CdWO_4$ single crystal of Φ25×90 mm. It is noticeable that the crystal is red at the top, gradated to dark brown at the lower end. A few cracks occurred in the as-grown crystals due to cleavage. The inset shows a photo of an as-grown sample and one annealed in O_2 at 1073 K. These Eu-doped samples came from the upper part of the crystal. The color becomes light red after O_2-annealing. This was attributed to the reduction of oxygen vacancies in the crystal.

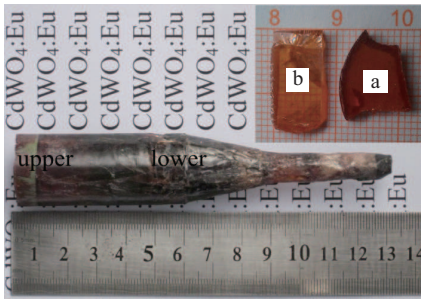


Fig. 1. (colour online) Photo of an Eu-doped $CdWO_4$ single crystal. The inset displays the upper part of unannealed sample a and sample b O_2-annealed at 1073 K.

The optical absorption spectra of undoped (dashed line) and Eu-doped (solid line) $CdWO_4$ crystals are shown in Fig. 2. Compared with the undoped sample, Eu doping increases the absorption gradually from 700 nm to 380 nm. Three small sharp absorption peaks at 396 nm, 465 nm, and 559 nm in Eu-doped crystals were observed, and those absorption bands were attributed to the $^7F_0 \rightarrow {}^5G_3$, $^7F_0 \rightarrow {}^5D_2$, and $^7F_0 \rightarrow S_5$ transition of Eu^{3+} ions.

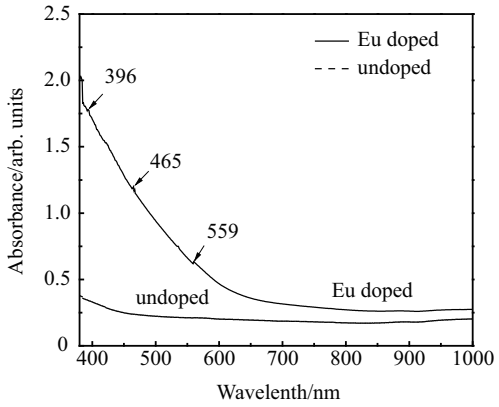


Fig. 2. Optical absorption of undoped (dashed line) and doped $CdWO_4$ crystal (solid line). The thickness of samples is 2.5 mm.

Figure 3 shows the excitation spectra of the Eu-doped crystal between 200 nm and 350 nm by monitoring the emissions at 464 nm and 614 nm, respectively. The two curves in Fig. 3 show similar characteristics. Both of them have a broad excitation band, and the bands can be decomposed into subcomponents by using Gaussian functions. The peaks of the two Gaussian functions are 266 nm and 310 nm, respectively. The band at 310 nm results from the emission of $CdWO_4$ single crystal.[19] The peak at 266 nm is very similar to those in other matrixes [7] and was attributed to the $^8S_{7/2} \rightarrow 4f^6 5d$ transition of Eu^{2+}. It indicates that Eu^{2+} ions exist in the $CdWO_4$ crystals.

Figure 4 shows the excitation spectra of the undoped (dashed line) and Eu-doped (solid line) crystals between 350 nm and 600 nm by monitoring the emission at 614 nm. Several sharp lines of $^5D_0$–^7F_J of Eu^{3+} ions in Eu-doped $CdWO_4$ crystal are observed at 363, 385, 396, 417, 465, and 535 nm, respectively. These lines are attributed to the f–f transitions of Eu^{3+}. Their detailed origins are displayed in Fig. 4.

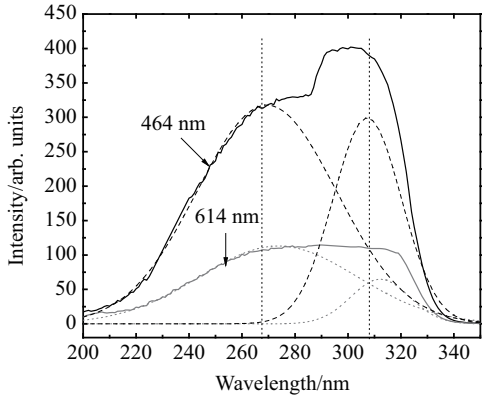


Fig. 3. Excitation spectrum of the Eu-doped $CdWO_4$ crystal at 200 nm–350 nm wavelengths monitored at 464-nm and 614-nm emissions.

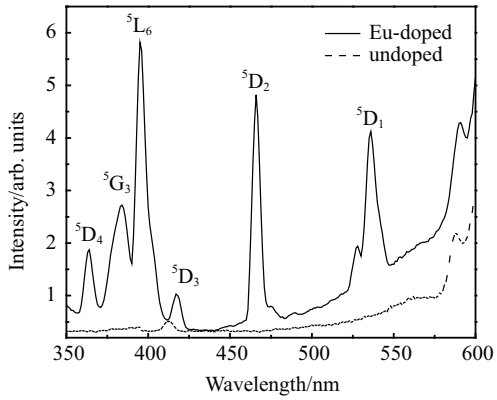


Fig. 4. Excitation spectrum of the undoped (dashed) and Eu-doped (solid) $CdWO_4$ crystals of 350 nm–600 nm wavelengths monitored at 614-nm emission.

Figure 5 shows the emission spectra of the undoped (dashed line) and Eu-doped $CdWO_4$ crystals under the excitation of a 266-nm light at room temperature. A broad band from 350 nm to 600 nm, and sharp lines at 614 nm and 589 nm can be observed in Fig. 5 for the Eu-doped $CdWO_4$ crystal. The sharp lines were attributed to the $^5D_0$–^7F_J transition of Eu^{3+} ions. Among them, the emission peak at 614 nm due to the $^5D_0 \rightarrow {}^7F_2$ transition was strongest. Note that a similar broad band at about 350 nm to 600 nm was also found for the undoped $CdWO_4$ crystal. By comparing the emission intensity of the broad band of those samples, one can see that the intensity of Eu-doped $CdWO_4$ is much stronger than that of the undoped. Therefore, one can conclude that the broad band is a result of the overlapping of the Eu^{2+} ion emission caused by the $4f^7$–$4f^6$5d transition of the emission of the $CdWO_4$ host crystal.

Many factors affect the valence state of the europium ions. Those factors include the processing technique and the structure/composition of the matrix. When Eu ions are added as a dopant, two Eu^{3+} ions substitute for three Cd^{2+} ions, and a cation vacancy defect with two negative charges is created. The cation vacancy acts as a donor of electrons and transfers electrons to Eu^{3+} in the crystal host during the growth process. As a result, the reaction of $Eu^{3+} + e^- \rightarrow Eu^{2+}$ occurs, and Eu^{2+} ions are formed. In addition, the crucible was sealed previously and kept sealed during crystal growth. This effectively cuts off any additional oxygen source during crystal growth. Because some ingredients such as CdO and WO_3 tend to be volatile at high temperature, a certain non-stoichiometry exists in the crystal. This non-stoichiometry is accompanied by oxygen vacancies (Vo'') Such an environment of oxygen deficiency and oxygen vacancies is a great advantage for the formation and stability of Eu^{2+} ions in $CdWO_4$ crystal. The excitation and emission spectra strongly indicate that the Eu^{3+} and Eu^{2+} coexist in the Eu-doped $CdWO_4$ crystal.

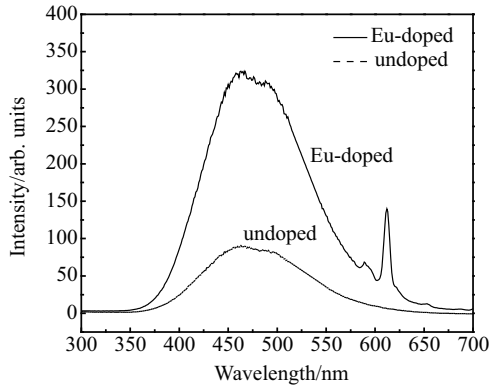


Fig. 5. Fluorescence spectra of the undoped (dashed line) and Eu-doped (solid line) $CdWO_4$ crystals.

3.2. The effect of O_2-annealing on optical spectra

It had been revealed that the annealing process had an important effect on the optical characteristics of the $CdWO_4$ crystals.[19,20] In order to investigate the relationships between the Eu^{2+} ions and oxygen vacancies, and the influence of O_2-annealing on the optical spectra of Eu-$CdWO_4$ crystal, the annealing treatment was carried out at different temperatures and atmospheres.

Figure 6 shows the comparison of excitation spectra of the O_2-annealed crystal at 1073-K and 1223-K temperatures, respectively. Excitation spectra were measured at an emission wavelength of $\lambda_{em} = 464$ nm. As previously discussed, the broad band was decomposed into two peaks at 266 nm and 310 nm of Gaussian functions. The intensity of the excitation band at 266 nm was weaker after the crystal was annealed at 1073 K. However, there was a slight decrease in the intensity of the excitation bands at 266 nm after the crystals were further

O_2-annealed at 1223 K. Also, it can be seen that the intensity of the excitation band at 310 nm increased slightly after the crystal was further O_2-annealed at 1073 K and 1223 K. The temperature-dependent behaviors of the spectra of $CdWO_4$ crystal in O_2-annealing was investigated previously.[20] We conclude that the reduction of oxygen vacancies is responsible for the increase in emission intensity of the excitation band at 310 nm. Hence, annealing can increase transparency and light yield.

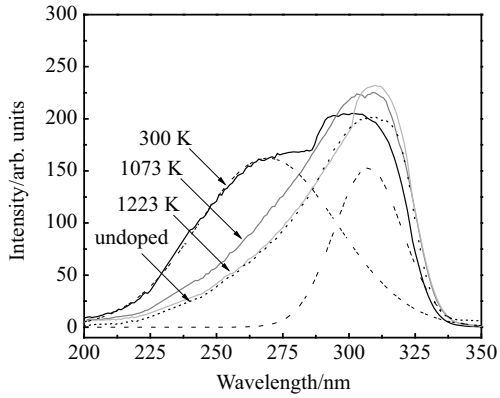


Fig. 6. Comparison of excitation spectra of the undoped (dotted line) and Eu-doped $CdWO_4$ crystals measured before and after O_2-annealing at 1073-K, 1223-K temperatures. The spectra were obtained by monitoring the $4f^6 5d–^8S_{7/2}$ emission at 464 nm.

As previously explained, oxygen vacancies are formed as a result of the non-stoichiometry caused by the volatilization of WO_3 and CdO during crystal growth. In order to reduce the oxygen vacancies and improve the crystal quality, the annealing process at various temperatures and atmospheres was carried out. Previous results indicate that annealing in any atmosphere below a temperature of about 973 K does not significantly affect the optical properties of $CdWO_4$ crystal. An optimal annealing process was carried out in oxygen at approximately 1223 K for about 24 hours. One can see that the as-grown Eu-doped $CdWO_4$ crystal is dark red, but the annealed crystal becomes light red. Both the excitation spectra and the emission spectra of the Eu-doped $CdWO_4$ crystal are changed after annealing. Luo *et al.*[19] has provided a possible mechanism of O_2-annealing temperature effects on the relevant defects in $CdWO_4$ crystal. The proposed mechanism of a change in the excitation band at 266 nm of Eu^{2+} ions with O_2-annealing temperature is as follows. When the annealing temperature is higher than 1073 K, oxygen diffuses into the crystal lattice and neutralizes some defects, such as oxygen vacancies. In the process, the Eu^{2+} ions are oxidized into Eu^{3+}, and the concentration of Eu^{3+} ions increases. Meanwhile, interstitial oxygen is also formed. As the annealing temperature further increases to about 1223 K, interstitial oxygen moves from the lattice to the surface of the crystal, resulting in stability of Eu^{2+} ions and holding a certain content of Eu^{2+} ions. The oxygen vacancies almost disappear as the temperature changes from 1073 K to 1223 K. The change of excitation spectra at 266 nm of Eu^{2+} in Fig. 6 fits well with the results of Eu^{2+} content in the annealing process.

Figures 7(a) and 7(b) compare the emission spectra of Eu-doped $CdWO_4$ crystal after annealing at 1073 K and 1223 K when excited by 396-nm and 266-nm lights, respectively. It can be seen from Fig. 7(a) that the emission intensity at 614 nm increases as annealing temperature increases when excited at 396 nm. This suggests that Eu^{2+} ions were converted into Eu^{3+} when annealed in O_2, increasing the Eu^{3+} content in the crystal. This matches well with the results of excitation spectra in Fig. 6. One can also see in Fig. 7(b) that the Eu^{3+} emission at 614 nm when excited at 266-nm light is significantly lower after annealing at 1073 K, but it only decreases slightly when further annealed at 1223 K. The same trend was observed for the 464-nm emission, which is attributed to the overlapping of Eu^{2+} emission and $CdWO_4$ host crystal emission. Figure 8 shows the relative emission intensities of Eu-doped $CdWO_4$ crystal at 614 nm and 464 nm after annealing when excited by 396-nm or 266-nm light.

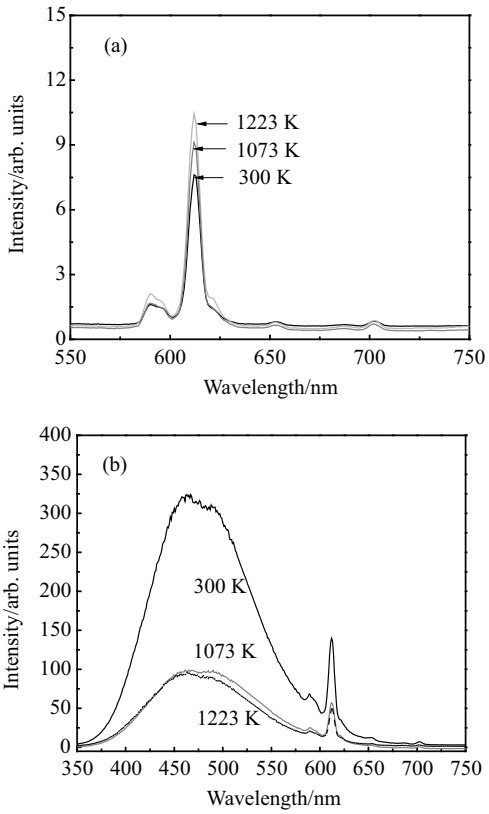


Fig. 7. Comparison of the fluorescence spectra of the Eu-doped $CdWO_4$ crystal annealed at various temperatures excited by a 396-nm (a) or 266-nm (b) light.

In others' work, the Eu^{3+} ion emission at 614 nm under excitation of 266 nm was observed in glasses containing both Eu^{2+} and Eu^{3+} ions.[21] This confirms the energy transfer from active Eu^{2+} to Eu^{3+} because there is no absorption

band for Eu^{3+} at 266 nm. Also, the changes of emission intensity related to Eu^{2+} and Eu^{3+} match well with the change of Eu^{2+} and Eu^{3+}content. This is a further validation of the energy transfer. During the energy transfer, the energy corresponding to the $4f^6$ 5d to $^8S_{7/2}$ transition of Eu^{2+} ions results in the excitation of the Eu^{3+} ions to the ^5D_J level when the crystal is excited by 266-nm light. As the annealing temperature increases from 300 K to 1223 K, the content of Eu^{2+} in $CdWO_4$ crystal decreases due to the conversion of Eu^{2+} ions to Eu^{3+} and the energy transfer between Eu^{2+} and Eu^{3+} ions becomes weak.

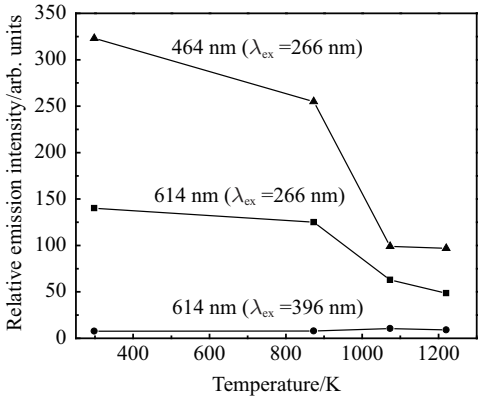


Fig. 8. The relationship between relative emission intensities of Eu-doped $CdWO_4$ crystal and their annealing temperature under excitement by 396-nm and 266-nm light.

4. Conclusion

The Eu ions can be doped into the $CdWO_4$ single crystal using the Bridgman method with appropriate process conditions, and the Eu ions exist in both +2 and +3 valent states in the crystal. The structure/composition of the $CdWO_4$ crystal is responsible for the existence of Eu^{2+} ions in the crystal. It is believed that oxygen vacancies are formed during the crystal growth process because of a non-stoichiometry caused by the combination of volatilization and the sealed condition of the crucible. The oxygen vacancies benefit the formation and stability of Eu^{2+} ions in the $CdWO_4$ crystal. The valence state of Eu^{2+} ions is affected by the post-growth O_2-annealing process. The content of Eu^{2+} ions in $CdWO_4$ crystal decreases as annealing temperature increases from 300 K to 1073 K due to the diffusion of oxygen into the crystal lattice. These additional oxygen anions compensate for the oxygen vacancies and effectively oxidize the Eu^{2+} ions into Eu^{3+}. However, this transition remained at a certain equilibrium level when the annealing temperature was further increased, due to the diffusion of interstitial oxygen from the lattice onto the surface of the crystal. The energy transfer occurs between Eu^{2+} and Eu^{3+} ions when the crystal is excited by 266-nm light, where the energy corresponding to the $4f^6$5d to $^8S_{7/2}$ transition of Eu^{2+} ions results in the excitation of the Eu^{3+} ions to the ^5D_J level.

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