Growth and optical properties of Cr³⁺-doped CdWO₄ single crystals

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A high-quality Cr³⁺:CdWO₄ single crystal at a size of approximately Φ 25×80 mm is grown using the Bridgman method with CdO, WO₃, and Cr₂O₃ as raw materials and their molar ratio of 100:100:0.5. The temperature gradient of solid-liquid interface at growth is approximately 50 °C/cm and the growth rate is 0.05 mm/h. The X-ray diffraction (XRD), absorption, excitation, and emission spectra of different parts of the as-grown and O₂-annealed crystals are investigated. Two strong broad optical absorption bands of about 472 and 708 nm are observed, and they are associated with the transitions $^4A_2 \rightarrow {}^4T_1$ and $^4A_2 \rightarrow {}^4T_2$. The weak $^4T_2 \rightarrow {}^2E$ transition (the R-line) at 632 nm is also observed. The crystal-field parameter Dq and the Racah parameters B and C are estimated to be 1 412.4, 776.8, and 3 427.6 cm⁻¹, respectively, according to the absorption spectra and crystal-splitting theory. A broadband fluorescence at about 1 000 nm due to $^4T_2 \rightarrow {}^4A_2$ transition is produced by exciting the samples at 675 nm. After being annealed in an O₂ atmosphere, the crystals become more transparent, while the effective light absorption of Cr³⁺ ions is evidently enhanced and the emission intensity is also strengthened due to the reduction of oxygen vacancies in the CdWO₄ crystal after annealing.

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Metal tungstates are important for their applications in scintillators and other optical devices[1]. In general, the properties of metal tungstates can be effectively modified by introducing cationic ions during the crystal growth. In recent years, metal tungstates doped with functional ions have been widely studied because they are competitive host materials in the optical field due to their promising applications for laser, phosphors, or scintillators[2].

CdWO₄ crystal is commercially viable and important among the metal tungstates. Previous studies have demonstrated that the Cd²⁺ site in the CdWO₄ tends to be occupied by cations with a low valence state, while the W⁶⁺ site tends to be replaced by cations with a higher valence state[3]. Active lanthanide ions (RE=Nd, Dy, Ho, Er, Tm or Yb) have been used as dopants to form active materials for laser purposes[2]. The Cr³⁺ ion is one of the transition metal ions used as activators in materials for tunable solid-state lasers[4]. Cr³⁺-doped crystals and optical properties have been reported[5−7]. Tunable solid-state lasers have a wide range of applications, such as medicine and life science, telecommunication, and environmental monitoring[8−10].

Almost all CdWO₄ single crystals were grown using the Czochralski (CZ) technique in previous works[11,12]. Some difficulties occur in this growing method for CdWO₄ single crystals. For instance, there is a continuous composition change of melts due to the volatilization of CdO and WO₃. In addition, cracking readily occurs in the as-grown crystals due to cleavage. We recently prepared CdWO₄ crystals using the Bridgman method[13]. In our process, harmful volatilization was minimized by sealing the crucibles, and the cracking of the crystals was reduced under other favorable conditions.

For the CdWO₄ crystals grown using the Bridgman method[13], we investigated their luminescence properties when doped with 0.5 mol% of Cr₂O₃. In addition, we studied their absorption, excitation, and emission spectra before and after O₂-annealing in order to explore their new applications as laser and scintillator materials.

The feed materials for Cr³⁺-doped CdWO₄ crystal growth were synthesized from highly pure CdO (99.99%) and WO₃(99.99%) with a molar ratio of 1:1. The mixtures were ground for 2 hours in a mortar and sintered at 1 150 °C for 5 hours in a furnace, yielding a white polycrystalline powder through solid state reaction. The 0.5% molar fraction of Cr₂O₃ (99.99%) dopant was mixed into the polycrystalline power. The mixtures were thoroughly ground and then charged into a platinum crucible where a seed of the CdWO₄ crystal with the *c*-axis direction was placed at the bottom. The crucible was quasi-sealed and then put into the furnace chamber for crystal growth.

The furnace chamber was gradually heated to 1 355 °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 material and the top of the seed were kept in a molten state for 3 hours, after which the crucible was pulled down at the rate of approximately 0.05 mm/h. The temperature gradient across the solid-liquid interface was from 50 to 60 °C/cm. This temperature gradient is beneficial for achieving high-quality crystals. Cr³⁺-doped CdWO₄ single crystal was grown in a similar manner as the undoped CdWO₄. The detailed procedures were previously reported[13]. Figure 1 shows a photo of the as-grown Cr³⁺-doped CdWO₄ single crystal that is 25 mm in diameter and 80 mm in length. The crystal was cut into small pieces and well polished to

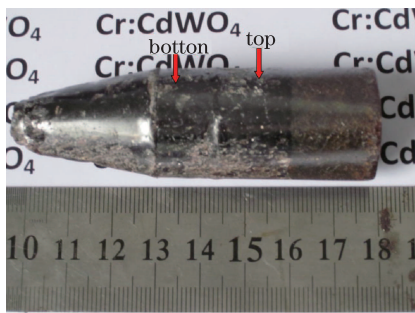Fig. 1. Photo of a Cr^{3+}-doped $CdWO_4$ crystal.

2.5 mm in thickness for optical measurement and annealing experiment.

Because it is easy for WO_3 and CdO to volatilize and the crystal was grown under quasi-sealed condition, numerous oxygen vacancies occurred in the as-grown crystals. Much of the literature mentioned the annealing of the $CdWO_4$ single crystal[14−16]. In order to reduce the oxygen vacancies and improve the crystal quality, the annealing treatment at different temperatures and atmospheres was carried out. The results showed that annealing in oxygen or air at 800 °C had a slight effect on the color and absorption characteristics of crystal. However, a remarkable change occurred when the annealing temperature was increased above 900 °C. A similar annealing process was previously reported for $CaWO_4$ crystals[17], and a similar result was observed. These studies demonstrated that annealing in any atmosphere below temperatures of 700 °C would not significantly affect the optical properties of the $CaWO_4$ crystal. The intensity of absorption bands evidently changed only when the annealing temperature was increased to above 700 °C. It has been proposed that, when the annealing temperature is higher than 700 °C, oxygen is able to diffuse into the crystal lattice and neutralize some defects, such as oxygen vacancies. Meanwhile, the interstitial oxygen O_i will also be formed. As the annealing temperature further increases to about 1 000 °C, O_i could move from lattice into the surface of the crystal, resulting in the change of absorption spectra and the transparency of the crystal. A similar mechanism applies to the Cr^{3+}-doped $CdWO_4$ crystal. The optimum annealing process was determined to be a combination of approximately 950 °C annealing temperature, oxygen atmosphere, and an annealing time of about 24 hours. Crystals were cooled to room temperature at 50 °C/h after the O_2-annealing process. Figure 2 shows a photo of as-grown and O_2-annealed Cr^{3+}-doped $CdWO_4$ crystal samples. It is noticeable that the as-grown Cr^{3+}-doped $CdWO_4$ crystal appears to be dark pink whereas the annealed crystal looks light pink.

The X-ray diffraction (XRD) spectra were obtained using a XD-98X diffractometer (XD-3, Beijing) with a Cu Kα radiation at 0.15406 μm. The optical absorption spectra were measured using a Perkin-Elmer Lambda 950 spectrophotometer in the wavelength region from 200 to 1 000 nm. The excitation and emission spectra were recorded on an F-4500 Spectrophotometer. All the measurements were carried out at room temperature.

The X-ray diffraction patterns of the as-grown and O_2-annealed Cr^{3+}-doped $CdWO_4$ crystals are shown in Fig. 3. The two curves were similar. By comparing the

peak positions with those in JCPDS84-0038 of cadmium tungstate, it was confirmed that the crystal was a single phase of $CdWO_4$. The result illustrated that doping with Cr^{3+} had no noticeable effect on the crystal phase. However, after annealing the treatment, the position of the diffraction peaks shifted slightly toward a lower 2θ value. This shift is evident through a careful comparison of the peak position between as-grown and O_2-annealed Cr^{3+}-doped $CdWO_4$ crystals, as shown in Fig. 3. The result suggests that the lattice constant of the crystal became slightly larger after annealing. This might be caused by the removal of thermal stress and reduction in oxygen vacancies during annealing. Moreover, the widths of the diffraction peaks became slightly narrow, and the intensity of the main diffraction plane (020) decreased sharply after annealing.

$CdWO_4$ has a typical wolframite-type structure. It belongs to the P2/c space group. Tungsten and cadmium atoms are within a highly distorted octahedron of oxygen atoms. Two oxygen ions of each octahedron are shared by adjacent octahedron, resulting in a chain-type structure. The chains of octahedron occur in a zigzag array[18]. The package of ABO_4 type crystal lattice does not practically permit the interstitial arrangement of impurity ions in $CdWO_4$ crystals. Therefore, the Cr^{3+} ions can replace either Cd^{2+} or W^{6+} ions in the octahedral neighborhood of oxygen ions. By comparing the radius of the Cd^{2+} ion (0.095 nm) and W^{6+} ion (0.060 nm) to that of the dopant ion (Cr^{3+}-0.096 nm), we believe that the occupation of Cd^{2+} cation sites by the Cr^{3+} ions is more favorable. In this case, a simple solution to maintain the lattice electrical neutrality is one Cd^{2+} vacancy for every two Cr^{3+} ions.

In the case of the Cr^{3+} ion placement on the W^{6+} site, the excess negative charge of –3 can be compensated by the neighboring oxygen vacancies with an effective charge
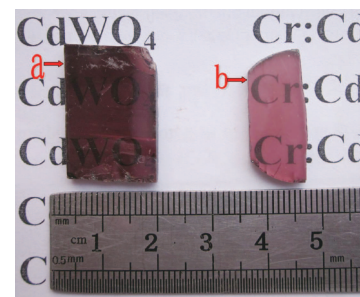

Fig. 2. Photo of Cr^{3+}-doped $CdWO_4$ crystal samples (a) before and (b) after O_2-annealing.
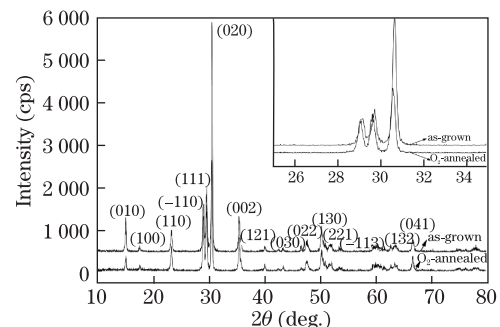

Fig. 3. XRD patterns of as-grown and O_2-annealed Cr^{3+}-doped $CdWO_4$ crystal.

of $+2$. Electrical neutrality is achieved through the formation of three oxygen vacancies for every two Cr^{3+} ions. The requirement to form a large amount of oxygen vacancy defects through this arrangement makes it less feasible[19].

Figure 4 shows the absorption spectra of the $CdWO_4$ crystal, the bottom section of an as-grown Cr^{3+}-doped $CdWO_4$ crystal boule, and both the top and bottom section of an O_2-annealed Cr^{3+}-doped $CdWO_4$ crystal boule. Figure 4(a) shows that the $CdWO_4$ crystal has excellent optical transmittance without any absorption band in the visible light region. However, as shown by Fig. 4(b), the as-grown Cr^{3+}-doped $CdWO_4$ crystal has intense absorption bands in the range from 400 to 800 nm. These absorption bands are caused by Cr^{3+} and other defects. After the O_2-annealing treatment, the intensity of absorption in the 400–600 nm range significantly decreased; at the same time, some absorption peaks related to Cr^{3+} became evident, as shown in Fig. 4(c) and (d). One can conclude that the emergence of Cr^{3+} absorption peaks is enabled by the reduction in absorption from oxygen-related defects. Such defects, including oxygen vacancies, are reduced by the annealing in the presence of O_2. The aforementioned oxygen vacancies were formed during the crystal growth process, which was carried out in an air-tight environment caused by the sealed crucible. As the crystal growth progresses, the partial pressure of oxygen decreases, and the atmosphere becomes oxygen deficient, leading to the formation of oxygen vacancies.

The absorption spectra are consistent with those reported in previous paper[5]. They are composed of two broad bands at wavelengths of about 472 and 708 nm, which are assigned to the $^4A_2 \to ^4T_1$ and $^4A_2 \to ^4T_2$ transitions of Cr^{3+} in the octahedral crystal field. The weak $^4T_2 \to ^2E$ transition (the R-line) at 632 nm can also be observed. Cr ions exist in the form of Cr^{3+} in the common lattice; no other characteristic absorption peaks related to Cr^{2+}[20] and Cr^{4+}[21] were observed in the absorption spectra. Therefore, it can be concluded that Cr ions exist in the $CdWO_4$ crystal only in the form of Cr^{3+}. On the other hand, the absorption coefficient of the top section of the crystal boule is higher than that of the bottom section of the boule. This indicates that the concentration of Cr^{3+} in the top section is higher th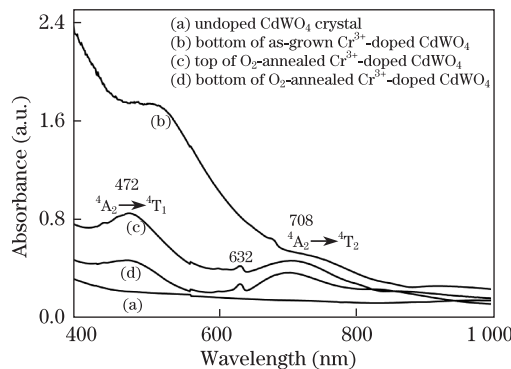an that of the bottom section. In other words, the concentration of Cr^{3+} increases along the crystal growth direction, which implies that the effective segregation coefficient of Cr^{3+} is less than 1 in $CdWO_4$ crystal.

Based on the absorption spectra of the annealed crystal and the crystal splitting theory, we can estimate the crystal-field parameter Dq and the Racah parameter B and C using the following equations[5]:

$$E(^4A_2 \to ^4 T_2) = 10Dq, \tag{1}$$

$$B = 0.33(2\nu_1 - \nu_2)\delta/(9\nu_1 - 5\nu_2), \tag{2}$$

$$E(^2E)/B = 3.05(C/B) + 7.9 - 1.8(B/Dq), \tag{3}$$

where ν_1 and ν_2 are the energy values at the peaks of the $^4A_2 \to ^4T_2$ and $^4A_2 \to ^4T_1$ absorption bands, respectively, δ is the energy separation between the peaks of these absorption bands, and $E(^2E)$ is the energy value of the ^2E energy level. Using these equations, the following values are obtained for Cr^{3+}-doped $CdWO_4$:

$$Dq \sim 1412.4 \ cm^{-1}; B \sim 776.8 cm^{-1};$$

$$Dq/B \sim 1.8; C \sim 3427.6 \ cm^{-1}.$$

The criterion for evaluation of the crystal fild strength is the value of the ratio between Dq and Racah parameter B(Dq/B). According to the Tanabe and Sugano diagram, for the $3d^3$ ions (Cr^{3+}), a strong crystal field is presented when Dq/B>2.3. In this case, the ^2E level lies lower than the $^4T_2$, and a sharp line emission occurs. When Dq/B<2.3, the crystal field is weak. Then the $^4T_2$ level is lower and a broadband luminescence is observed. In addition, materials in intermediate field of Dq/B occur at about 2.3. In this study, the Dq/B ratio of 1.8 shows that Cr^{3+}-doped $CdWO_4$ belongs to the low-field site crystals, and the lowest excited state is $^4T_2$. The crystal-field parameter Dq and the Racah parameter B and C of other Cr^{3+}-doped crystals are listed in Table 1.

Figure 5 shows the excitation and emission spectra of top and bottom sections of the O_2-annealed crystal boule. It also shows those of the bottom section of the as-grown crystal boule. Excitation spectra were measured at an emission wavelength of $\lambda_{em}=1000$ nm. An excitation band at 675 nm is observed in Fig. 5(a). The emission spectra are recorded by exciting the samples at 675 nm, as shown in Fig. 5(b). A broad emission band from 920 to 1070 nm was presented and peaked at around 1000 nm due to the $^4T_2 \to ^4A_2$ transition[22]. The full-width at half-maximum (FWHM) is of the order of 85 nm. The bandwidth of near-infrared fluorescence depends on the interaction between the Cr^{3+} and crystal field around it[6]. The Cr^{3+} ion-doped $CdWO_4$ crystal with broadband emission provides the possibility for developing a tunable solid laser in the near-infrared region[23].

Fig. 4. (a) Absorption spectra of $CdWO_4$, (b) bottom section of as-grown Cr^{3+}-doped $CdWO_4$, (c) top section, and (d) bottom section of O_2-annealed Cr^{3+}-doped $CdWO_4$.

Table 1. Values of Crystal-Field Parameter Dq, Racah Parameters B and C of Cr^{3+} Ions in Crystals

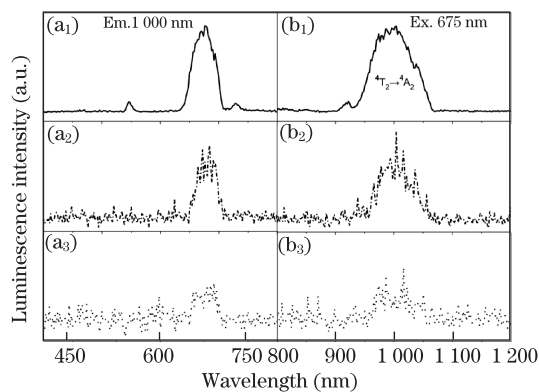| Crystals	$Dq(cm^{-1})$	$B(cm^{-1})$	$C(cm^{-1})$	Dq/B
Cr^{3+}:$LiNbO_3$[15]	1 522	596	3 890	2.67
Cr^{3+}:$BeAl_2O_4$[15]	1 764	608	3 371	2.9
Cr^{3+}:$NaAl(WO_4)_2$[5]	1 548	615.6	3 083	2.51
Cr^{3+}:$KZClSO_4 \cdot 3H_2O$[16]	1 724	724	2 484	2.38
Cr^{3+}:$ZnWO_4$[17]	1 329	745	3 680	1.78
This Letter	1 412.4	776.8	3 427.6	1.8

Fig. 5. (a_1) Excitation spectra of top section and (a_2) bottom section of O_2-annealed, (a_3) bottom section of as-grown Cr^{3+}-doped $CdWO_4$ crystal; (b_1) emission spectra of top section and (b_2) bottom section of O_2-annealed, and (b_3) bottom section of as-grown Cr^{3+}-doped $CdWO_4$ crystal.

The intensity of both the excitation and emission spectra of the bottom crystal section is higher after annealing compared with that of the as-grown crystal. The enhancement of the excitation and emission can also be explained by the reduction of oxygen vacancies when the crystal is annealed in the oxygen atmosphere, as previously described.

By comparing excitation and emission spectra of the annealed crystal shown in Fig. 5, it is evident that the fluorescence intensity of the top section is higher than that of the bottom section. Since the higher fluorescence intensity is associated with higher Cr^{3+} concentration, this further confirms that the effective segregation coefficient of Cr^{3+} is less than 1 in the $CdWO_4$ crystal.

In conclusion, the Cr^{3+} ion can be effectively doped into the $CdWO_4$ crystal using the Bridgman method with appropriate process conditions. The Cr^{3+} ion is likely to replace the Cd^{2+} ion that lies in the octahedral neighborhood of the oxygen O^{2-} ions. A broadband fluorescence (FWHM of approximately 85 nm) at about 1 000 nm due to $^4T_2 \rightarrow {}^4A_2$ transition is measured by exciting the samples at 675 nm. Oxygen vacancies are formed during the crystal growth and can be removed by annealing the crystal in oxygen or air. As the amount of oxygen vacancies is reduced by annealing in an oxygen-rich atmosphere at 950 °C, the Cr^{3+} ions in the crystal can absorb more photon energy from the excitation light source, which enhances the fluorescence intensity at 1 000 nm. The crystal-field parameter Dq and the Racah parameter B and C are estimated to be 1 412.4, 776.8, and 3 427.6 cm^{-1}, respectively, and the Dq/B value of 1.8 shows that $CdWO_4$ medium provides a low-field for Cr^{3+}. The effective segregation coefficient of Cr^{3+} is less than 1 in the $CdWO_4$ crystal.

References

1. D. Ye, D. Li, W. Chen, Y. Shao, G. Xiao, M. Sun, and X. Fu, Res. Chem. Intermed. **35,** 675 (2009).
2. M. Guzik, E. Tomaszewicz, S. M. Kaczmarek, J. Cybińska, and H. Fuks, J. Non-Cryst. Solids **356,** 1902 (2010).
3. N. Y. Garces, M. M. Chirila, H. J. Murphy, J. W. Foise, E. A. Thomas, C. Wicks, K. Grencewicz, L. E. Halliburton, and N. C. Giles, J. Phys. Chem. Solids **64,** 1195 (2003).
4. H. Xia, H. Song, J. Wang, J. Zhang, T. Wang, J. Zhang, Y. Zhang, and Q. Nie, Cryst. Res. Technol. **40,** 199 (2005).
5. I. Nikolov, X. Mateos, F. Güell, J. Massons, V. Nikolov, P. Peshev, and F. Díaz, Opt. Mater. **25,** 53 (2004).
6. E. Cavalli, A. Belletti, and M. G. Brik, J. Phys. Chem. Solids **69,** 29 (2008).
7. I. Sokólska and S. Kück, Spectrochim. Acta Part A **54,** 1695 (1998).
8. G. Wang, X. Long, L. Zhang, G. Wang, S. Polosan, and T. Tsuboi, J. Lumin. **128,** 1556 (2008).
9. H. Teng, S. Zhou, H. Lin, T. Jia, X. Hou, and J. Wang, Chin. Opt. Lett. **8,** 414 (2010).
10. Q. Fang, H. Chen, F. Xu, S. Wang, Z. Liang, and C. Jiang, Chin. Opt. Lett. **8,** 1071 (2010).
11. H. Xiao, H. Chen, F. Xu, C. Jiang, and P. Yang, J. Chin. Ceramic Soc. (in Chinese) **36,** 617 (2008).
12. A. Vedda, F. Moretti, and M. Fasoli, Phys. Rev. B **80,** 045104 (2009).
13. H. Xiao, H. Chen, F. Xu, C. Jiang, and P. Yang, J. Cryst. Growth **310,** 521 (2008).
14. H. Chen, H. Xiao, F. Xu, C. F. Xu, C. Jiang, and P. Yang, J. Inorganic Materials (in Chinese) **24,** 1036 (2009).
15. H. Chen, Q. Shen, Q. Fang, H. Xiao, S. Wang, Z. Liang, and C. Jiang, J. Synthetic Crystals (in Chinese) **39,** 829 (2010).
16. L. Luo and Y. Wang, J. Quantum Electronics (in Chinese) **25,** 166 (2008).
17. V. Yakovyna, A. Matkovskii, D. Sugak, I. Solskii, and S. Novosad, Radiat. Meas. **38,** 403 (2004).
18. Y. Abraham, N. A. W. Holzwarth, and R. T. Williams, Phys. Rev. B **62,** 1733 (2000).
19. K. Tanaka, K. Ohga, C.-K. Choo, and R. Nakata, J. Appl. Phys. **90,** 5369 (2001).
20. Y. Yang, J. Xu, and Y. Hang, Laser & Optoelectronics Progress (in Chinese) **144,** 50 (2007).
21. M.Y. Sharonov, A. B. Bykov, S. Owen, V. Petricevic, and R. R. Alfano, J. Appl. Phys. **93,** 1044 (2003).
22. H. Xia, J. Wang, H. Wang, J .Zhang, Y. Zhang, and H. Song, Rare Metals. (in Chinese) **29,** 181 (2005).
23. W. Kolbe, K. Petermann, and G. Huber, IEEE J. Quantum Electron. **21,** 1596 (1985).