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RE:KYb$(WO_4)_2$(RE=Nd^{3+},Er^{3+})激光晶体生长与结构特性

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摘 要: 采用泡生法(Kyropoulos method)生长了稀土掺杂钨酸镱钾[RE:KYb$(WO_4)_2$, RE=Nd^{3+},Er^{3+}]激光晶体, 并对其结构特性进行了研究。RE:KYb$(WO_4)_2$晶体是由 WO_6, REO_8 和 KO_{12} 3 种基团组成, W_2O_{10} 二聚体通过 WOW 单氧桥相连, 在平行于 c 轴方向上形成$(W_2O_8)_n$多重带。REO_8 和 KO_{12} 多面体共顶相连, 沿[101]和[110]方向形成了具有二维层结构的延长带。X 射线粉末衍射分析表明: Nd^{3+}:KYb$(WO_4)_2$ 和 Er^{3+}:KYb$(WO_4)_2$ 两种晶体具有低温 β 相 RE:KYb$(WO_4)_2$ 结构, 属于单斜晶系, 空间群为 $C2/c$, 计算了晶格常数。晶体红外光谱测试结果表明: 在 630~930 cm^{-1} 范围存在 5 个较强的红外吸收峰, 这些吸收峰是由 WO_4 基团的伸缩振动引起的。最后, 对峰值与相应的振动模式进行了归属, 证实了晶体中 WOOW 双氧桥和 WOW 单氧桥键的存在。

关键词: 掺钕钨酸镱钾; 掺铒钨酸镱钾; 激光晶体生长; 泡生法; 结构特性
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GROWTH AND STRUCTURE CHARACTERISTICS OF RE(Nd^{3+},Er^{3+})-DOPED POTASSIUM YTTERBIUM TUNGSTATE LASER CRYSTAL

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Abstract: RE:KYb$(WO_4)_2$ (RE=Nd^{3+}, Er^{3+}) crystals were grown by the Kyropoulos method, and their structural characteristic was investigated. The structure of the crystals is composed of three kinds of groups, including WO_6, REO_8 and KO_{12} polyhedrons. The W_2O_{10} dimmers are connected by WOW single oxygen bridging bonds and form $(W_2O_8)_n$ bands along c axis in parallel direction. The REO_8 and KO_{12} polyhedrons in the crastals are joined by common vertex and form an elongated band with the structure of two-dimensional layer along [101] and [110] directions. Then powder X-ray diffraction analysis indicates that the two crystals of Nd^{3+}:KYb$(WO_4)_2$ and Er^{3+}:KYb$(WO_4)_2$ belong to a monoclinic system with a space group $C2/c$, which indicates that the crystals obtained are β-RE:KYb$(WO_4)_2$. The cell parameters of the two crystals were calculated, too. The infrared spectra show that they have five strong infrared absorption peaks from 630 to 930 cm^{-1}, which were caused by stretching vibration of WO_4 groups. Finally, the vibration modes and frequencies were identified, which confirmed the existence of WOOW double oxygen bridge and WOW single oxygen bridge bonds in the crystals.

Key words: potassium ytterbium tungstate doped by neodymium ions; potassium ytterbium tungstate doped by erbium ions; laser crystal growth; Kyropoulos method; structure characteristics

The double tungstates of $KM(WO_4)_2$ (M=Y and Ln) as a laser host materials has attracted considerable attention due to its excellent properties,[1] such as $KGd(WO_4)_2$ (KGW), $KY(WO_4)_2$ (KYW), $KYb(WO_4)_2$, $KDy(WO_4)_2$, $KHo(WO_4)_2$, *etc*. The potassium ytterbium tungstate [$KYb(WO_4)_2$, KYbW]crystal is a member of this family. It belongs to monoclinic structure with space group $C2/c$, cell parameters $a=1.059$ nm, $b=1.029$ nm, $c=0.748$ nm, $\beta=130.7°$, $Z=4$.[2] It is an excellent laser crystal because its refractive coefficient changes little with temperature and has high quantum efficiency, which can result in super-speed pulse laser output of application power. In order to obtain the laser output of different wavelengths, KYbW crystal can be used as host when doped with some

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rare earth ions (RE), such as Nd^{3+}, Er^{3+}, Tm^{3+} and so on. Compared to RE:KGW and RE:KYW crystals, quantities of Yb^{3+} ions in KYbW host can be used as sensitizer ions to increase the absorption light and then transfer the energy to RE^{3+} ions so as to achieve laser output of different wavelengths. Due to its low symmetry, it can be doped with high concentrations of rare earth ions and can also be used in slice or microchip lasers, which are very important for the integration, miniaturization and compactness of laser diode (LD) pumped solid-state lasers.[3–5]

In this work, RE:KYbW (RE=Nd^{3+}, Er^{3+}) crystals were grown by the Kyropoulos method, and their structural characteristics were investigated.

1 Experimental procedure

1.1 Material preparation

Since RE:KYbW crystals have a phase transition below melting point, it generally must be grown by the flux method. $K_2W_2O_7$ was selected as a mixed flux because of its several merits.[6] The chemicals used were high purity-grade K_2CO_3, WO_3, Nd_2O_3, Er_2O_3 and Yb_2O_3 with a purity of 99.99% in mass. They were mixed and reacted as the following equations:

$$K_2CO_3+0.05Nd_2O_3+0.95Yb_2O_3+4WO_3 \longrightarrow 2KNd_{0.05}Yb_{0.95}(WO_4)_2+CO_2\uparrow \quad (1)$$

$$K_2CO_3+0.1Er_2O_3+0.9Yb_2O_3+4WO_3 \longrightarrow 2KEr_{0.1}Yb_{0.9}(WO_4)_2+CO_2\uparrow \quad (2)$$

$$K_2CO_3+2WO_3 \longrightarrow K_2W_2O_7+CO_2\uparrow \quad (3)$$

where the mole ratio of $K_2W_2O_7$ as solvent to $KRE_xYb_{1-x}(WO_4)_2$ (RE=Nd^{3+}, Er^{3+}, x=0.05, 0.1) was 4:1. After the materials had been dried in an oven for 24 h, an electronic balance was used to mix the ingredients at the right proportion with an accuracy of 0.1 mg, and then the raw materials were mixed evenly and porphyrized for reservation. In order to avoid volatilizing, the matched materials should be calcined in advance. The solvent was removed at 600 ℃ since the melting point of $K_2W_2O_7$ was about 619 ℃. The RE:KYbW polycrystal materials were obtained after calcined at 920℃ for 8h.

1.2 Crystal growth

The RE:KYbW (RE=Nd^{3+}, Er^{3+}) crystals were grown by the Kyropoulos method. The polycrystal material placed in the platinum crucible with a size of 60 mm in diameter and 50 mm height in a resistance wire furnace (type MCGE–III) was fully melted at 80 ℃ above supersaturation temperature for 12 h. The temperature was measured and controlled by a Pt–Rh thermocouple, and an AI–808P thermal controller. Then a *b*-oriented seed with dimension of 3 mm × 3 mm × 12 mm was put into the melt. After seeding, the furnace temperature was decreased to 5 ℃ above the supersaturation temperature. Then the growth continued with following parameters seen from Table 1.

1.3 Measurement of samples

The crystal structures were analyzed by a X-ray diffractometer (XRD, Model D/max–rA, Rigaku), using a Cu K_α ray (λ = 0.154 056 nm) as the radiant, and with a tube voltage of 50 kV and a tube current of 150 mA, and with a graphite monochromator. The infrared (IR) spectra of the crystals were measured using a Fourier conversion IR spectroscopy (Model FTS135, BIO–RAD company) with a distinguish ability of 4 cm^{-1} and a scanning rate of 64 times/s.

Table 1 The growth parameters of RE:KYbW (doped RE = Nd^{3+}, Er^{3+}) crystals

Crystal	Doping mole fraction/%	Seeding temperature/℃	Rotating rate/($r \cdot min^{-1}$)	Cooling growing rate/($℃ \cdot h^{-1}$)	Annealing rate/($℃ \cdot h^{-1}$)	Growth period/d	Crystal size/mm^3
Nd:KYbW	5	918	15	0.10	30	15	28 × 15 × 10
Er:KYbW	10	890	10	0.05	25	20	25 × 15 × 10

2 Results and discussion

2.1 Powder XRD analysis

The results of powder XRD analysis of RE:KYbW (RE = Nd^{3+}, Er^{3+}) crystals are shown in Fig.1. Compared with the standard diffraction pattern of JCPDS card (54–0249), the diffraction patterns show that the diffraction peaks and relative intensity of the two crystals are very similar to those of pure β-KYbW. Therefore, the two crystals belong to a monoclinic phase with a space group *C*2/*c*, which indicates that two crystals obtained are β-RE:

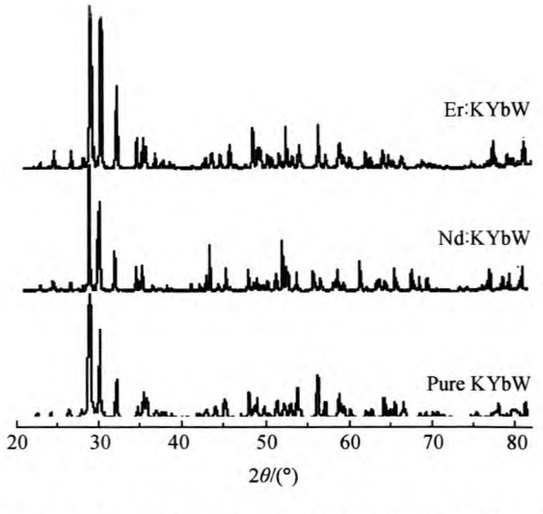


Fig.1 Powder XRD patterns of RE:KYbW (RE=Nd^{3+}, Er^{3+}) crystals

KYbW. According to formula (4) below for cell parameters of monoclinic systems, the cell parameters of two crystals are calculated and listed in Table 2.

$$d=\frac{ABC\sin\beta}{\sqrt{A^2B^2+B^2C^2+A^2C^2\sin^2\beta-2AB^2C\cos\beta}} \quad (4)$$

where A, B, and C are defined as the intercept of the crystal plane whose distance is the minimum on a, b, and c axes, and the distance is from the (hkl) family of crystal planes to the original point, where $A=a/h$, $B=b/k$ and $C=c/l$.

Table 2　Cell parameters of the RE:KYbW (RE=Nd^{3+}, Er^{3+}) crystals

Sample	Doping ionic radius/nm	a/nm	b/nm	c/nm	β/(°)	Z
KYbW[2]	0.094 (Yb^{3+})	1.059	1.029	0.748	130.70	4
Nd:KYbW	0.103 (Nd^{3+})	1.063	1.031	0.749	130.63	4
Er:KYbW	0.096 (Er^{3+})	1.061	1.031	0.749	130.65	4

Z is molecular number of unit cell.

2.2　Crystal structure

According to crystal structure information obtained from XRD patterns, the software of crystal structure analysis was used to plot crystal structure model of RE:KYbW, as seen from Figs.2 and 3. The RE:KYbW crystal with low temperature phase belongs to monoclinic system with a space group $C2/c$. Figure 2 shows the projection graphs of the structure of RE:KYbW crystal along a, b, c and (111) directions, respectively. It can be seen from the graphs that WO_6 distorted octahedron can be formed by means of the coordination between one wolframium atom and six oxygen atoms, and wolframium atoms occupy C_1 symmetric position. Figure 3(a) is the partially enlarged graph of WO_6 distorted octahedron. Due to the interaction of wolframium atoms, W_2O_{10} dimmer can be formed through the connection of WOOW double oxygen bridge. The W_2O_{10} dimmers are also joined by WOW single oxygen bridging bonds and form $(W_2O_8)_n$ bands along c axis in parallel direction. The $(W_2O_8)_n$ bands are joined by common edges, and the partially enlarged graph can be seen from Fig.3(b). The REO_8 polyhedrons can be formed by means of the coordination between one rare earth atom and eight oxygen atoms, and Fig.3(c) is the partial enlargement graph of REO_8 polyhedrons. Meanwhile, the KO_{12} polyhedrons can be formed by means of the coordination between one potassium atom and twelve oxygen atoms, and Fig.3(d) shows the partially enlarged graph of KO_{12} polyhe- drons. The potassium and rare earth atoms together occupy C_2 symmetric position by means of statistical distribution. The REO_8 eight-coordinated polyhedrons and KO_{12} twelve- coordinate polyhedrons are joined by common vertex and form an elongated band with the structure of two dimensional layer along [101] and [110] directions, and the elongated band fills into the framework made up of rare earth and WO_6 octahedron groups. As a result, the structure of RE:KYbW crystals are very similar to that

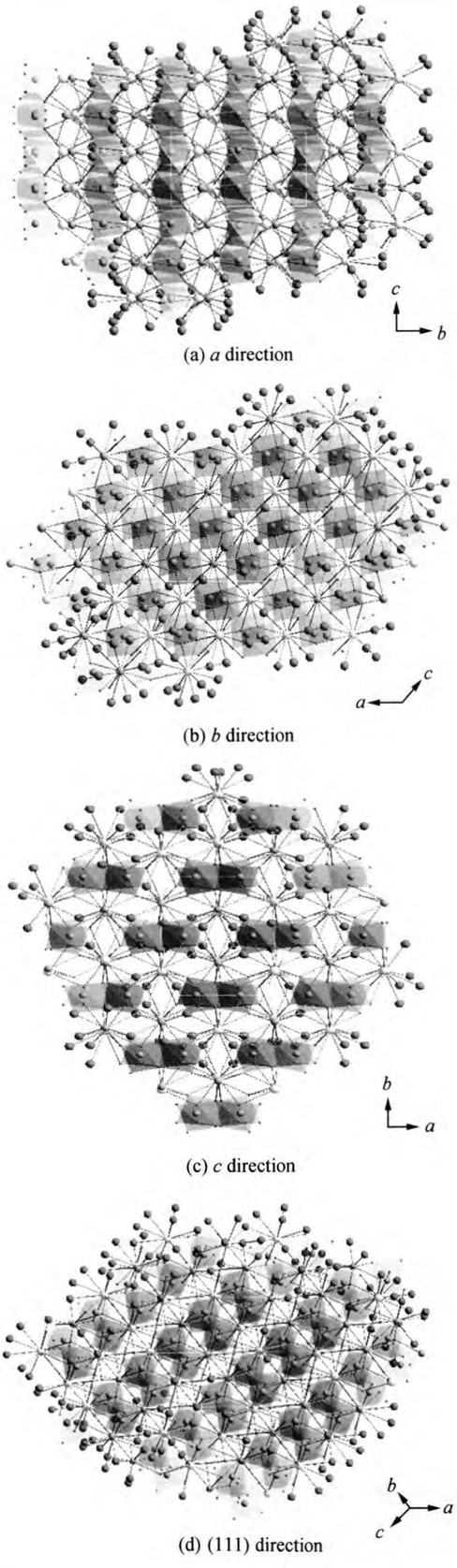
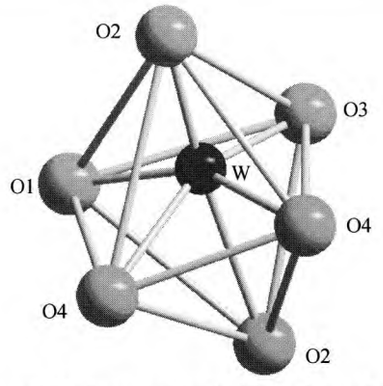
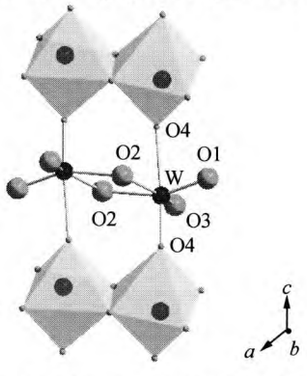


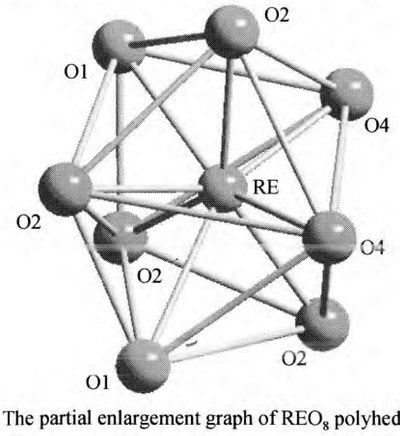
Fig.2　The projection graphs of the structure of RE:KYbW crystals along a, b, c and (111) directions



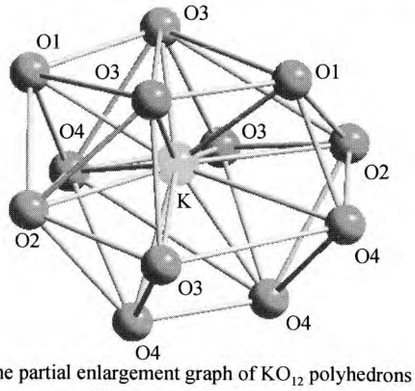
(a) The partial enlargement graph of WO_6 distorted octahedron



(b) The partial enlargement graph of $(W_2O_8)_n$ bamds



(c) The partial enlargement graph of REO_8 polyhedrons



(d) The partial enlargement graph of KO_{12} polyhedrons

Fig.3 The partially enlarged graphs of WO_6 distorted octahedron, $(W_2O_8)_n$ bands, REO_8 polyhedrons and KO_{12} polyhedrons

of RE:KYW[7] and RE:KGW[8] crystals. The difference of crystal structure between RE:KYbW and RE:KYW/KGW is that interatomic distances of them are different because of different ionic radius.

2.3 IR spectra of crystals

The IR spectra of the two crystals can be seen in Fig.4. The vibration frequency range of WO_4 group is 900–750 cm^{-1} (stretching vibration) and 420–300 cm^{-1} (bending vibration).[9] From the curve of Nd:KYbW crystal, the IR absorption peaks at 635, 774, 839, 891, 925 cm^{-1} can be attributed to the stretching vibration of WO_4 group. The IR absorption peak at 479 cm^{-1} shows the wagging vibration of WO_4 group. It also indicates that some water came into the sample when the sample was placed in the air, so the IR absorption peaks at 3 452 and 1 640 cm^{-1} (1 400 cm^{-1}) belong to the asymmetric stretching and bending vibration of the O–H bond. As for the IR curve of Er:KYbW crystal, the IR absorption peaks at 634, 779, 847, 891, 926 cm^{-1} are the result of the stretching vibration of WO_4 group. The IR absorption peak at 484 cm^{-1} shows the wagging vibration of WO_4 group. The IR absorption peaks at 3 460 and 1 630 cm^{-1} (1 400 cm^{-1}) belong to the asymmetric stretching and bending vibration of the O–H bond. Table 3 lists the IR

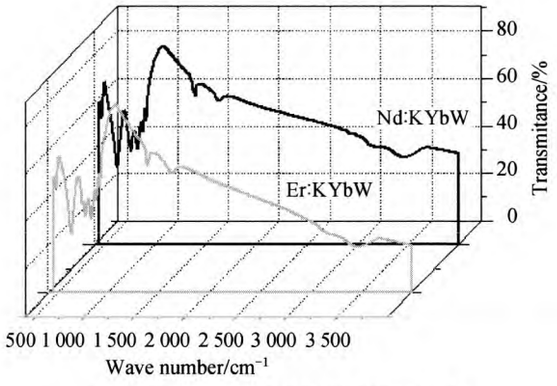


Fig.4 IR spectra of RE:KYbW crystals

Table 3 IR spectra vibration frequencies assignment of RE:KYbW (RE = Nd^{3+}, Er^{3+}) crystals

Assignment	IR absorption peak/cm^{-1}	
	Nd:KYbW	Er:KYbW
ω(WOOW)	479	484
ν_s(WOOW)	635	634
ν(WOOW)	774	779
$\nu_{as}(WO_6)+\nu_{as}$(WOW)	839	847
$\nu_s(WO_6)+\nu$(WOOW)	891	891
$\nu_s(WO_6)$	925	926
δ_{as}(OH)	1 400	1 400
	1 640	1 630
ν_{as}(OH)	3 452	3 460

Notes: ω—Wagging vibration; ν_s—Symmetric stretching vibration; ν—Stretching vibration; ν_{as}—Asymmetric stretching vibration; δ_{as}—Asymmetric bending vibration.

spectra vibration frequencies assignment of two crystals. The results of IRS confirm the existence of WOOW double oxygen bridge and WOW single oxygen bridge bonds in RE:KYbW crystals.

3 Conclusions

The RE:KYbW(RE=Nd^{3+}, Er^{3+}) laser crystals were obtained by the Kyropoulos method, with $K_2W_2O_7$ as solvent. The crystal growth conditions were as follows: rotation rate was 10–15 r/min, cooling growing rate was 0.05–0.1 ℃/h, annealing rate was 25–30 ℃/h, and the growth period was 15–20 d. The structure of RE: KYbW crystals is composed of three kinds of groups, including WO_6, REO_8 and KO_{12} polyhedrons. The W_2O_{10} dimmers are connected by WOW single oxygen bridging bonds and form $(W_2O_8)_n$ bands along *c* axis in parallel direction. The REO_8 and KO_{12} polyhedrons are joined by common vertex and form an elongate band with the structure of two-dimensional layer along [101] and [110] directions. The two crystals have a β-RE:KYbW structure with a low thermal phase. The cell parameters of the Nd:KYbW and Er:KYbW crystals calculated are $a_1=1.063$ nm, $b_1=1.031$, $c_1=0.749$, $\beta_1=130.63°$, $Z_1=4$; $a_2=1.061$ nm, $b_2=1.031$, $c_2=0.749$, $\beta_2=130.65°$, $Z_2=4$, respectively. The IR spectra show that they have five strong IR absorption peaks from 630 to 930 cm^{-1}, which are caused by stretching vibration of WO_4 groups. The results of IR analysis confirm the existence of WOOW double oxygen bridge and WOW single oxygen bridge bonds in RE:KYbW crystals.

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