Growth, Structure and Spectroscopic Characterization of Nd$^{3+}$-Doped KBaGd(WO$_4$)$_3$ Crystal with a Disordered Structure

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Abstract

The undoped and the Nd$^{3+}$:KBaGd(WO$_4$)$_3$ crystals were grown by the top seeded solution growth (TSSG) method from a flux of K$_2$W$_2$O$_7$. The structure of the pure crystal was determined by the single-crystal X-ray diffraction method. It crystallizes in the monoclinic symmetry with space group $C2/c$. In the structure, K$^+$ and Ba$^{2+}$ ions share the same 8f site with occupancy of 0.464 and 0.536, respectively. The investigation of spectral properties of Nd$^{3+}$:KBaGd(WO$_4$)$_3$ crystal indicates that it exhibits broad absorption and emission bands, which are attributed to locally disordered environments around the Nd$^{3+}$ centers. The broad absorption band is suitable for diode laser pumping.

Introduction

The diode-laser pumped solid-state lasers are useful in a wide variety of applications in the fields of military [1,2], industry [3] and medical treatments [4] due to their advantages, such as outstanding stability, high efficiency, compact size and long lifetime. A lot of well-known Nd$^{3+}$-doped laser crystals (Nd:YAG, for example [5]) are commercially available, however, they can be hardly pumped with diode-lasers. Because they have very narrow absorption bands near their pumped wavelength compared to the emission bandwidths of common diode-lasers (several nanometers), they cannot absorb the pump energy of diode-lasers efficiently. Besides, the temperature stability of the emission wavelength of diode-lasers needs to be crucially controlled for laser crystals with narrow absorption bands, since the emission wavelength of the diode-lasers changes at 0.2–0.3 nm/K with the operating temperature of the laser device. [6] As a consequence, it is necessary to explore novel laser crystals with large absorption bandwidths for diode pumping.

The broadening of the spectral features can be expected for solid-state materials with multisites, defects, or local disorder [7]. In the past few years, there have been a lot of studies on the family of scheelite-related disordered molybdate and tungstate crystals $\text{AT}$(XO$_4$)$_2$ ($\text{A}=\text{monovalent Li, Na}; \text{T}=\text{trivalent Bi, Y, La-Lu};$ $\text{X}=\text{Mo, W}$) [8–10]. These disordered crystals have been demonstrated as promising materials in the domains of tunable and ultrashort femto-second laser pulse due to the obvious advantage of large spectral broadening. Recently, we synthesized a new triple tungstate KBaGd(WO$_4$)$_3$ compound also with disordered structure. Because of the mixed K$\text{Ba}$ occupancy of the same crystallographic site, 8f, the structure of KBaGd(WO$_4$)$_3$ presents some local disorder around Gd$^{3+}$ sites, and thus can lead to the spectral broadening when rare-earth luminescent ions (such as Nd$^{3+}$) replace Gd$^{3+}$. Therefore, this paper reports on the growth, structure and spectral properties of Nd$^{3+}$-doped KBaGd(WO$_4$)$_3$ crystal.

Materials and Methods

1. Synthesis and Crystal Growth

Polycrystalline samples of undoped KBaGd(WO$_4$)$_3$ were synthesized by means of the solid-state reaction method. The synthesis process followed that of ref. [11]. To evaluate melting point of the synthesized KBaGd(WO$_4$)$_3$ compound, the thermal analysis was carried out by differential scanning calorimetry (DSC) using a NETZSCH STA 490C Simultaneous Thermal Analyzer, which was performed up to 1563 K at a heating and cooling rate of 15 K min$^{-1}$.

The undoped and Nd$^{3+}$:KBaGd(WO$_4$)$_3$ crystals were grown by the top seeded solution growth method. The crystal growth was carried out in a vertical tubular furnace, as shown in Fig. 1. An AL-708 controller with controlling accuracy of ±0.1 K was used to control the furnace temperature and the cooling rate.

2. Crystal Structure Analysis

A single crystal of undoped KBaGd(WO$_4$)$_3$ with dimensions of 0.10×0.10×0.10 mm$^3$ was selected for X-ray diffraction determinations. The diffraction data were collected on a Mercury70 CCD diffractometer equipped with graphite-monochromated Mo Kα ($\lambda=0.71073$ Å) radiation at 293 K. A total of 1214 independent reflections were collected in the range of 3.35° < $\theta$ < 27.45°, of
which 1102 with $I \geq 2\sigma(I)$ were independent. The absorption correction based on the empirical PSI-scan technique was applied. The structure was solved by direct methods and refined by the full-correction based on the empirical PSI-scan technique was applied. The final unweighted residual factor which is used to judge the structure model is 0.0229. The weighted residual factor $wR$ is 0.0514 with the weighting factor $w = 1/(\sigma^2(F_o^2) + (0.0268P)^2 + 0.0000P)^{1/2}$, where $P = (F_o^2 + 2F_c^2)/3$, in the above equations, $\sigma(F_o^2)$ is the estimated standard uncertainty of the observed reflections, $F_o^2$ and $F_c^2$ means the observed and calculated squared structure factors, respectively. After the refinement, the residual electron density $\Delta \rho_{\text{max}} = 1.542$, and $\Delta \rho_{\text{min}} = -2.045$ $\rho/\rho_0$, $\Delta(\sigma/\sigma_0)_{\text{max}} = 0.000$. The value of goodness of fit $\chi^2$ which is used to adjust the weighting scheme is 1.050. The details of the X-ray structure analysis are listed in (Table S1). The X-ray power diffraction (XRD) pattern of undoped KBaGd(WO$_4$)$_3$ was determined using a D-max-rA type diffractometer with Cu K$\alpha$ radiation ($\lambda = 1.54056$ $\AA$) at room temperature. The power electron diffraction pattern of undoped KBaGd(WO$_4$)$_3$ crystal was carried out by a JEM-2010 transmission electron microscope.

### 3. Spectral Characterization

Since Nd$^{3+}$-KBaGd(WO$_4$)$_3$ crystal with the monoclinic system is optically biaxial, three optical indicatrix axes ($X$, $Y$, $Z$) should be determined before the measurement of polarized spectra. One of the optical indicatrix axes ($Y$) is parallel to the unique two-fold crystallographic axis ($b$-axis, which is also the $C_2$ symmetry axis), and the other two lie in a perpendicular plane to this axis. The orientation of the crystal was performed by means of crossed polarized microscope, and the orientating procedure follows that of ref. [13]. The $c$-axis is at 16° anticlockwise with respect to the indicatrix $Z$-axis, and the angular relationship between the optical indicatrix axes and the crystallographic axes ($a$, $b$, $c$) for Nd$^{3+}$-KBaGd(WO$_4$)$_3$ crystal is shown in Fig. 2. After orientation, a sample with dimensions of 5.5×3.8×2.6 mm$^3$ and high optical quality was cut from the as-grown crystal, as shown in Fig. 3 (c).

The polarized absorption spectra were measured with a Perkin-Elmer UV-VIS-NIR spectrophotometer (Lambda 900). Excited by a continuous Xe-lamp at 805 nm, the polarized emission spectra were recorded using an Edinburgh Instruments FLS920 spectrophotometer. All the spectral experiments were carried out at room temperature. In spectral experiment, the electric field of the light is parallel to each one of the three optical indicatrix axes, $E \parallel X$, $E \parallel Y$, and $E \parallel Z$.

### Results and Discussion

#### 1. DSC Analysis and Crystal Growth

The DSC result reveals that the undoped KBaGd(WO$_4$)$_3$ crystal melts incongruently (Fig. 4). In the heating cycle, an endothermic peak corresponding to a solid-liquid transformation is observed, which means the KBaGd(WO$_4$)$_3$ is decomposed at 1372 K, and then melts completely to form the liquid phase at 1477 K. The cooling curve shows two exothermic peaks with maxima at 1463 K and 1355 K, respectively, with the second one corresponding to resolidification of KBaGd(WO$_4$)$_3$.

Since the KBaGd(WO$_4$)$_3$ crystal exists a phase transition at temperatures lower than the melting point, hence the best technique to grow it is the top seeded solution growth method (TSSG) [14]. The Nd$^{3+}$-KBaGd(WO$_4$)$_3$ crystal was grown in a flux of K$_2$W$_2$O$_7$ by this method, where the molar ratio of KBaGd(WO$_4$)$_3$ to K$_2$W$_2$O$_7$ is 1:1. The chemical used were K$_2$CO$_3$, BaCO$_3$, WO$_3$ with analytical-grade as well as Gd$_2$O$_3$ and Nd$_2$O$_3$ with 99.99% purity. According to their stoichiometric composition, 3.0 at % Nd$^{3+}$-doped KBaGd(WO$_4$)$_3$ and K$_2$W$_2$O$_7$ were weighed. The weighed materials were mixed and put in a platinum crucible with a volume of 100 mm$^3$. The mixture was slowly heated up to 1273 K in air atmosphere, and then maintained at that temperature for 48 hours to achieve a homogeneous melt. The saturation temperature of the solution was determined by repeated seeding. The starting growth temperature was about 1203 K. The crystals were grown at a cooling rate of 1K/day and a rotating rate of 45 rpm. When the growth ended, the grown crystals were carefully withdrawn from the solution and cooled to room temperature at 15 K h$^{-1}$. The Nd$^{3+}$-KBaGd(WO$_4$)$_3$ crystal with few inclusions and dimensions of 21×24×12 mm$^3$ was obtained, as shown in Fig. 3 (a). The morphology of the crystal is shown in Fig. 3(b), which was

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**Figure 1. Schematic diagram of crystal growth apparatuses:** (1) seed holder; (2) Al$_2$O$_3$ tube; (3) melt; (4) thermocouple; (5) crucible; (6) thermal insulation material; (7) seed.

**Figure 2. Relative orientation between the optical indicatrix axes ($X$, $Y$, $Z$) and the crystallographic axes ($a$, $b$, $c$) of the Nd$^{3+}$-KBaGd(WO$_4$)$_3$ crystal.** The plot means view from the positive $b$-axis direction.

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**Figure 2. Relative orientation between the optical indicatrix axes ($X$, $Y$, $Z$) and the crystallographic axes ($a$, $b$, $c$) of the Nd$^{3+}$-KBaGd(WO$_4$)$_3$ crystal.** The plot means view from the positive $b$-axis direction.

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simulated with Bravais-Friedel and Donnay-Harker based WinX-Morph software. [15].

The composition of the grown crystal was measured in an inductively coupled plasma by atomic emission spectrometry (ICP-AES) technique. For this purpose, the Nd\(^{3+}\):KBaGd(WO\(_4\))\(_3\) sample was heated at 363 K and dissolved in 37\% HCl, then the signal of ICP intensity was quantified from the comparison of the standard elements and corrected by the calibration curve. The result of ICP is listed in Table 1. The measured molar ratio K: Ba: (Gd+Nd): W is close to 1:1:1:3, which agrees with the composition of Nd\(^{3+}\):KBaGd(WO\(_4\))\(_3\) compounds.

2. Crystal Structure

Fig. 5(a) shows the XRD pattern of undoped KBaGd(WO\(_4\))\(_3\) crystal that can be indexed on the basis of lattice parameters. The indexed result of power electron diffraction pattern of undoped KBaGd(WO\(_4\))\(_3\) crystal is in agreement with that of the powder X-ray diffraction pattern, as shown in Fig. 5(b), which confirmed the XRD result. The powder XRD data of undoped KBaGd(WO\(_4\))\(_3\) crystal are listed in Table S2.

The crystallographic analysis of the undoped KBaGd(WO\(_4\))\(_3\) crystal reveals that it crystallizes in the monoclinic system with space group C2/c. The lattice parameters of KBaGd(WO\(_4\))\(_3\) crystal are: \(a = 17.544(4)\) Å, \(b = 12.174(16)\) Å, \(c = 5.320(9)\) Å, \(\beta = 105.498(11)^\circ\), and \(V = 1095.0(3)\) Å\(^3\) (also see CIF file: CIF S1). The atomic coordinates and thermal parameters are given in Table S3. In the refined structure, the Gd and W(2) fully occupy \(8f\) sites, and W(1) as well as the eight types of O are found in different \(8f\) sites. After least-squares refinement, the valence charge equilibrium and the magnitude of temperature factors demonstrate the existence of a statistic distribution of K and Ba, in single \(8f\) sites with occupancy factors fixed to 0.464:0.536, which shows that KBaGd(WO\(_4\))\(_3\) crystal has a high disordered structure.

The crystalline structure is constituted by K/BaO\(_8\) distorted square antiprisms with \(C_1\) symmetry, distorted GdO\(_8\) polyhedra which form chains lying along the \(c\)-axis (see Fig. 6 (a)) and two kinds of distorted WO\(_4\) tetrahedra. It can be described as layers stacked along the \(a\)-axis formed by corrugated six-membered rings of disordered K/BaO\(_8\) polyhedra, which share edges (Fig. 6 (b)). Adjacent layers are connected through distorted WO\(_4\) polyhedra and GdO\(_8\) chains (Fig. 7). The distinctive layered arrangement further increases the locally variable crystal field around Gd sites. The Gd\(^{3+}\) ions could provide appropriate sites for Nd\(^{3+}\) replacements because the Gd\(^{3+}\) and Nd\(^{3+}\) ions have the same valence, and additionally offer multiple distributions of cationic environments around these sites due to the coexistence of K\(^+\), Ba\(^{2+}\) and Gd\(^{3+}\) ions. Therefore, when Nd\(^{3+}\) replaces Gd\(^{3+}\) ions, the high disordered environment around the Nd\(^{3+}\) dopant ions leads to inhomogeneous broadening of the absorption and emission bands [16,17].

Figure 3. (a) Nd\(^{3+}\):KBaGd(WO\(_4\))\(_3\) crystal grown by TSSG method. (b) Stimulated facets marked by Miller indices (hkl). (c) An orientated rectangle sample cut from the as-grown crystal. Each face is perpendicular to one of the optical indicatrix axes.

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Figure 4. DSC curves of undoped KBaGd(WO\(_4\))\(_3\) compound.
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### Table 1. Summary of the elemental analysis results of 3.08 at% Nd\(^{3+}\)-doped KBaGd(WO\(_4\))\(_3\) crystal by the ICP-AES technique.

| Elements | W       | K       | Ba  | Gd | Nd |
|----------|---------|---------|-----|----|----|
| Required (Wt%) | 51.22  | 3.63    | 12.75 | 14.02 | 0.54 |
| Measured (Wt%)  | 50.96±1.02 | 3.27±0.07 | 12.43±0.25 | 13.84±0.28 | 0.43±0.009 |
| Calculated molar number (10\(^{-2}\)) | 27.72±0.55 | 8.36±0.18 | 9.05±0.18 | 8.80±0.18 | 0.30±0.006 |
| Molar ratio | 3.06±0.12 | 0.92±0.038 | 1±0.04 | 0.97±0.039 | 0.0309±0.0013 |

\(^*\)the Gd\(^{3+}\) ions were generally substituted by Nd\(^{3+}\) ions in the Nd\(^{3+}\)-doped KBaGd(WO\(_4\))\(_3\) crystal because the Gd\(^{3+}\) and Nd\(^{3+}\) ions have the same valence.

3. Spectral Properties

Fig. 8 shows the polarized absorption spectra of the Nd\(^{3+}\)-doped KBaGd(WO\(_4\))\(_3\) at room temperature. These absorption lines are due to transition from the ground state \(4I_9/2\) to the various excited states of Nd\(^{3+}\) ions. In the absorption spectra, the most interesting is the broad absorption bands in the range of 780–840 nm, which is close to the output wavelength of commercially diode laser devices. The absorption spectra are strongly polarization dependent because of the anisotropy of the monoclinic crystal. The absorption spectrum for \(E||Y\) polarization is strongest among the three absorption spectra and it has a full-width at half-maximum (FWHM) of 14 nm at 803 nm, which is larger than that of the ordered crystal, like Nd\(^{3+}\):BaGd\(_2\)(MoO\(_4\))\(_4\) crystal (4 nm, \(E||Z\) or LaB\(_3\)O\(_6\) (5 nm, \(E||X\)) [18,19]. Such large FWHM caused by the highly disordered structure around Nd\(^{3+}\) centers is suitable for diode-laser pumping. This demonstrates the Nd\(^{3+}\)-doped KBaGd(WO\(_4\))\(_3\) crystal can be pumped effectively and not restricted to the temperature stability of the output wavelength of diode-laser.

The absorption cross-section \(\sigma_a\) was calculated using the \(\sigma_a = \alpha / N_c\) formula, where \(\alpha\) is the absorption coefficient and \(N_c\) is the concentration of Nd\(^{3+}\). The concentration of Nd\(^{3+}\) ions in Nd\(^{3+}\)-doped KBaGd(WO\(_4\))\(_3\) crystal was measured to be 3.08 at% (i.e. 1.12 \(\times 10^{-20}\) cm\(^{-3}\)), and the results of the \(\sigma_a\) are listed in Table 2.

The emission cross-sections were calculated using the Fröhlich-Ladenbauer (F-L) equation, [20].

\[
\sigma_q^e = \frac{\lambda^2 A_q(J-J')I_q(\lambda)}{8\pi c n^2 \int_q(\lambda)d\lambda}
\]

where \(I_q(\lambda)\) is the emission intensity at wavelength \(\lambda\) with \(q\) polarization, \(A_q\) is the emission probability which can be calculated from the Judd-Olfelt theory [21,22], the refractive index \(n\) is calculated to be 1.83 using the method mentioned in Ref. [23].

Fig. 9 shows the wavelength dependences of the stimulated emission cross-sections. Three emission bands observed at 850–950, 1020–1150 and 1300–1450 nm are due to the transitions of \(4F_{3/2} \rightarrow 4I_{9/2}\), \(4F_{3/2} \rightarrow 4I_{11/2}\) and \(4F_{3/2} \rightarrow 4I_{13/2}\), respectively. The most important transition of \(4F_{3/2} \rightarrow 4I_{11/2}\) is centered at about 1060 nm. The FWHM for \(E||Y\) polarization is 24 nm, which is much larger than that of ordered structure crystals (see Table 2).

The peak stimulated emission cross-sections for the transition of \(4F_{3/2} \rightarrow 4I_{11/2}\) are 4.5, 6.5 and 4.1 \(\times 10^{-20}\) cm\(^2\) for \(E||X, E||Y\) and \(E||Z\), respectively.

![Figure 5](https://example.com/figure5.png)

**Figure 5.** (a) Powder XRD patterns of undoped KBaGd(WO\(_4\))\(_3\) crystal. (b) Powder electron diffraction pattern of the undoped KBaGd(WO\(_4\))\(_3\) crystal.

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4. Conclusion

The 3.08 at% Nd$^{3+}$-doped KBaGd(WO$_4$)$_3$ crystal was successfully grown by the TSSG method. The thermal analysis shows it melts incongruently at 1372 K. The structure analysis indicates that the undoped KBaGd(WO$_4$)$_3$ crystal has a statistic distribution of K(0.464) and Ba(0.536) atoms. Each Ba(K) is coordinated by eight oxygen atoms to form a distorted polyhedron. This fact and its layered arrangement structure lead to locally disordered environments around the Gd$^{3+}$ ions. When Gd$^{3+}$ ions are substituted by Nd$^{3+}$ dopant ions, the disordered structure results the broad FWHM of absorption and emission bands. Such broad FWHM of absorption band is suitable for diode-laser pumping. The Nd$^{3+}$:KBaGd(WO$_4$)$_3$ crystal with broad FWHM of emission band is promising as a candidate for tunable and short pulse solid-state laser operation. The spectroscopic properties of the Nd$^{3+}$:KBaGd(WO$_4$)$_3$ crystal are anisotropic with the largest absorption and emission cross sections for $E \parallel Y$ polarization. The Nd$^{3+}$:KBaGd(WO$_4$)$_3$ crystal has large absorption and emission cross-sections, which are $6.9 \times 10^{-20}$ cm$^2$ at 805 nm and $6.5 \times 10^{-20}$ cm$^2$ at 1060 nm respectively.

Supporting Information

Table S1 Crystal data and structure refinement details for undoped KBaGd(WO$_4$)$_3$.

Table S2 Powder XRD data of undoped KBaGd(WO$_4$)$_3$ crystal.

Table S3 Atomic coordinates and thermal parameters for undoped KBaGd(WO$_4$)$_3$ crystal.

CIF S1 The CIF file of the undoped KBaGd(WO$_4$)$_3$ crystal.

Author Contributions

Conceived and designed the experiments: BX GW. Performed the experiments: BX ZL. Analyzed the data: BX GW. Contributed reagents/materials/analysis tools: YH LZ. Wrote the paper: BX GW.
Table 2. Comparison of spectral parameters of Nd$^{3+}$:KBaGd(WO$_4$)$_3$ with other Nd$^{3+}$-doped laser crystals.

| Crystal            | Polarization | Absorption ($\sim$805nm) | Emission ($\sim$1060 nm) | Disordered | Ref.  |
|--------------------|--------------|---------------------------|--------------------------|------------|-------|
|                    |              | FWHM | $\sigma_x$  (10$^{-20}$ cm$^2$) | FWHM | $\sigma_x$  (10$^{-20}$ cm$^2$) |       |       |
| KBaGd(WO$_4$)$_3$  | $E||X$       | 11   | 4.5             | 19  | 4.5             |       |       |
|                    | $E||Y$       | 14   | 6.9             | 24  | 6.5             | Yes   | [24]  |
|                    | $E||Z$       | 19   | 4.1             | 19  | 4.1             |       |       |
| LiLa(WO$_4$)$_2$   | $\pi$-polarization | 20   | 2.2             | –   | 8.9             | Yes   | [24]  |
|                    | $\sigma$-polarization | 20   | 2.8             | –   | 7.8             |       |       |
| NaY(WO$_4$)$_2$    | $\pi$-polarization | 17   | –              | $\approx$ 13 | –              | Yes   | [25]  |
|                    | $\sigma$-polarization | 17 | –              | $\approx$ 13 | –              |       |       |
| KBaGd(MoO$_4$)$_3$ | unpolarized  | 9    | 11.1            | 24  | 5.17            | Yes   | [16]  |
| BaGd$_2$(MoO$_4$)$_4$ | $E||X$       | –    | 4.3             | 4   | 8.6             |       |       |
|                    | $E||Y$       | –    | 3.3             | 4   | 7.2             | No    | [18]  |
|                    | $E||Z$       | 4    | 17.5            | 3   | 19.2            |       |       |
| LaB$_3$O$_6$       | $E||X$       | 3    | 5.0             | 4   | 10.2            |       |       |
|                    | $E||Y$       | 3    | 4.5             | 3   | 8.3             | No    | [19]  |
|                    | $E||Z$       | 4    | 5.5             | 4   | 7.2             |       |       |

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