Growth, Structure, Thermal Properties and Spectroscopic Characteristics of Nd$^{3+}$-Doped KGdP$_4$O$_{12}$ Crystal

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Abstract

A single crystal of Nd$^{3+}$-doped KGdP$_4$O$_{12}$ was successfully grown with the top-seeded solution growth and slow cooling (TSSG—SC) technique. It crystallizes in space group C2/c with cell parameters $a = 7.812(2)$ Å, $b = 12.307(3)$ Å, $c = 10.474(2)$ Å, $\beta = 110.84(3)^\circ$ and $Z = 4$. The IR and Raman spectra also indicated that the phosphoric polyhedra of Nd:KGdP$_4$O$_{12}$ has a cyclic symmetry. The chemical composition of the crystal was analyzed and the distribution coefficient of Nd$^{3+}$ was calculated. The crystal morphology of KGdP$_4$O$_{12}$ was identified using X-ray diffraction. The compound has good thermal stability to 920°C. Its specific heat and thermal conductivity were determined for potential applications. The spectral properties of Nd:KGdP$_4$O$_{12}$ indicates that it exhibits broad absorption and emission bands, which are attributed to low symmetry of the crystal. The broad absorption band around 798 nm has a full-width at half-maximum (FWHM) of 14.8 nm and is suitable for AlGaAs laser diode pumping. Moreover, 5 at% Nd$^{3+}$-doped KGdP$_4$O$_{12}$ crystal has a long luminescence lifetime of 300 μs and a high quantum efficiency of 96%.

Introduction

With the development of the diode-pumped solid-state (DPSS) laser materials based on neodymium-doped crystals, research on new laser host materials has gained much interest [1]. Nd:YAG crystal is still the most common Nd$^{3+}$ laser material because of its good physical and laser properties, but it is limited to low Nd$^{3+}$-doped concentration and narrow absorption bandwidth near the AlGaAs diode emission wavelength of 808 nm. Because the emission wavelength of the laser diode increases at 0.2–0.3 nm K$^{-1}$ of the laser device, the temperature stability of the laser diode needs to be tightly controlled. Therefore, it is necessary to explore new and more efficient crystals for DPSS lasers. Furthermore, the absorption band of laser crystals close to the laser output of more efficient crystals for DPSS lasers. Furthermore, the absorption band around 798 nm has a full-width at half-maximum (FWHM) of 14.8 nm and is suitable for AlGaAs laser diode pumping. Moreover, 5 at% Nd$^{3+}$-doped KGdP$_4$O$_{12}$ crystal has a long luminescence lifetime of 300 μs and a high quantum efficiency of 96%.

The authors have declared that no competing interests exist.

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AlGaAs laser diode pumping. Moreover, 5 at% Nd$^{3+}$-doped KGdP$_4$O$_{12}$ crystal has a long luminescence lifetime of 300 μs and a high quantum efficiency of 96%.
with Nd$^{3+}$. Second, raw materials for preparing KGdP$_4$O$_{12}$ are easily available and very cheap in comparison with double metaphosphates of cesium or rubidium. Third, the spectroscopic spectrum of doped active ions may be broadened because of its low symmetry in the space group $C2/c$. Finally, the KGdP$_4$O$_{12}$ crystal has a cyclic geometry that is difficult to cleave in contrast with compounds having long chain geometry.

To the best of our knowledge, the crystal growth of KGdP$_4$O$_{12}$ has not yet been reported. Here, we have grown a single crystal of Nd$^{3+}$-doped KGdP$_4$O$_{12}$ with high quality and determined its structural character to be a cyclic geometry via single crystal structural analysis and IR and Raman spectroscopy. The spectral characteristics of the Nd:KGdP$_4$O$_{12}$ crystal were studied through its absorption spectrum, emission and excitation fluorescent spectra, and fluorescence decay curve. Finally, we measured its thermal stability, specific heat and thermal conductivity.

Materials and Methods

1. Crystal growth

The crystal growth used a single-zone vertical tubular electric furnace with a Kantal AF heater. The temperature of the furnace was measured near the heater with a B-type thermocouple and regulated with a SHIMADEN FP21 type temperature controller.

We grew Nd:KGdP$_4$O$_{12}$ crystals with the top-seeded solution growth and slow cooling (TSSG-SC) technique from a self-flux. The starting material was prepared by mixing Nd$_2$O$_3$ (4N), Gd$_2$O$_3$ (4N), K$_2$CO$_3$ (99.0%) and NH$_4$H$_2$PO$_4$ (99.0%) at a molar ratio of 0.05:0.95:3:12 in an agate mortar. This was then transferred into a 0.05:0.95:3:12 mm$^2$ Pt crucible to melt in batches. During the melting, a stoichiometric Nd$_2$O$_3$, Gd$_2$O$_3$, K$_2$CO$_3$ and NH$_4$H$_2$PO$_4$ generated the title compound KGd$_{0.95}$Nd$_{0.05}$P$_4$O$_{12}$. An excess of K$_2$CO$_3$ and NH$_4$H$_2$PO$_4$ reacted to produce potassium metaphosphate compound, which served as a self-flux to avoid foreign ions during the crystal growth. The typical chemical reactions are shown below.

$$K_2CO_3 + 0.95Gd_2O_3 + 0.05Nd_2O_3 + 8NH_4H_2PO_4 \rightarrow 2K_{0.95}Nd_{0.05}P_4O_{12} + 8NH_3 \uparrow + CO_2 \uparrow + 12H_2O \uparrow$$

$$K_2CO_3 + 2NH_4H_2PO_4 \rightarrow 2KPO_3 + 2NH_3 \uparrow + CO_2 \uparrow + 3H_2O \uparrow$$

There was marked bubbling of NH$_3$, CO$_2$ and H$_2$O and the mixture was heated slowly to a melt. The melt was homogenized at 900°C with a stirrer until the melt was clear and there were no bubbles. Meanwhile, the crucible was rotated alternately clockwise and counterclockwise at 15 revolutions per minute for complete homogenization. The oscillating crucible rotation was also necessary during the crystal growth for effective mass transport. The coldest position in the solution was 0.5 cm below the melt surface and the temperature gradient in the axial direction was 1.3°C·cm$^{-1}$. After several attempts, the melt temperature decreased to 812°C. Meanwhile, a thick wire of platinum attached to a corundum rod was introduced into the furnace and was placed above the melt. About 10 min later, the platinum wire was immersed below the melt surface as a seed. While maintaining the oscillating crucible rotation, the melt temperature was reduced at 0.4°C·d$^{-1}$ until it reached 794°C. During this process, the solute first crystallized on the platinum wire, which served as the seed for larger crystals.

After the growth was completed, the crystals were removed from the solution. The furnace was cooled to room temperature slowly and then some single crystals clustering around the platinum wire were taken out of the furnace. Figure 1(a) shows that the biggest one of these had good transparency with no cracks or inclusions. The colour of the crystal shows that the neodymium ion had already entered the crystal lattice. The stoichiometry of the crystal was analyzed by inductively coupled plasma—atomic emission spectrometer (ICP—AES) (Thermo IRIS Advantage). The density of the Nd:KGdP$_4$O$_{12}$ crystal at room temperature (23°C) was measured using a density unit of Sartorius balance (YDK01-C) by the buoyancy method.

2. X-ray diffraction analysis

The X-ray diffraction (XRD) technique was used to analyze several aspects of the as-grown Nd:KGdP$_4$O$_{12}$ single crystal such as determining its structure, identifying the crystalline phase, studying the crystal morphology as well as crystallinity.

A single crystal of Nd:KGdP$_4$O$_{12}$ cut from the as-grown crystal was used for indexing and intensity data collections on a Rigaku Saturn CCD area detector diffractometer using Mo Kα graphite monochromated radiation (λ = 0.71073 Å). The structure was resolved with the SHELXS-97 computer utility, and refined by a full-matrix least-squares method with SHELXL-97 software.

Polycrystalline powder of Nd:KGdP$_4$O$_{12}$ was prepared from the as-grown single crystal. The powder X-ray diffraction (PXRD) pattern of Nd:KGdP$_4$O$_{12}$ was recorded at room temperature with a Fangyuan DX2700 (Dandong, China) powder diffractometer using graphite monochromated Cu Kα radiation in the 2θ range 10°—70° with a step of 0.02°.

An XRD goniometer was used to identify and orientate the crystalline forms that comprised the morphological habit for the

Figure 1. Photograph (a) of the as-grown single crystal with a size of 20 mm×10 mm×5 mm and the theoretical morphology (b) of the Nd:KGdP$_4$O$_{12}$ crystal.

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as-grown single crystal had well-developed facets. XRD was also used to check the quality of the as-grown Nd:KGdP$_4$O$_{12}$ crystal. The crystal in Figure 1(a) was polished and used as a sample. The rocking curve of the (004) diffraction crystal face was obtained on an XRD diffractometer (PANalytical X’Pert PRO) equipped with a four-crystal Ge (022) monochromator. The setting of the X-ray tube (PW3373/10) was 40 kV and 10 mA. The step time and step size were 0.1 s and 0.001°, respectively.

3. IR and Raman spectroscopy

The molecular spectroscopy and lattice vibrations of Nd:KGdP$_4$O$_{12}$ were studied with Fourier transform infrared (FTIR) and Raman spectroscopy. The IR spectrum of a KBr pressed pellet of the powered sample was recorded from 4000 to 400 cm$^{-1}$ on a Nicolet Magna-IR 560 ESP FTIR spectrometer. The as-grown crystal shown in Figure 1(a) was also studied on a Renishaw inVia Raman microscope. The output wavelength of the excited CW argon laser was 514 nm.

4. Thermal analysis

The thermal stability of Nd:KGdP$_4$O$_{12}$ was measured with both thermogravimetry and differential scanning calorimetry (TG–DSC) using a Netzsch STA 449C from 40 to 1000°C at 10°C·min$^{-1}$. The specific heat of the Nd:KGdP$_4$O$_{12}$ crystal was also measured by DSC using a simultaneous thermal analyzer (Netzsch DSC 200 F3) in an atmosphere of N$_2$.

The thermal diffusivity was measured by the laser flash method using a laser flash apparatus (Netzsch LFA 457 Nanoflash) in the temperature range at intervals of 50°C. A 0.95 mm×4 mm×4 mm sample was used to carry out the measurements whose {001} faces were polished and coated with graphite on both sides.

5. Spectroscopic characterization

A 4.30-mm thick sample was polished and used to measure the spectroscopic properties. The polished facet was {001}. The unpolarized absorption spectrum was measured on a Hitachi UV−Vis−NIR spectrophotometer (U4100) from 175 to 2000 nm. The fluorescence spectra were recorded using an Edinburgh Instruments FLS920 spectrophotometer with a xenon lamp as the excitation source. The incident light and fluorescence were dispersed with two M300 monochromators using ruling gratings from Bentham Instruments. A cooled Hamamatsu R5509-72 photomultiplier was used for detection. The decay curve was measured using a pulsed xenon lamp as the pump source. The pulse duration was 10 ns, and the excitation wavelength was 808 nm. All the measurements were performed at room temperature (300 K). The splitting of the Nd$^{3+}$ emission band was also studied at 10 K using the same FLS920 spectrophotometer equipped with a close cycle helium cryostat (Advanced Research Systems DE202).

Results and Discussion

1. Crystal growth and chemical composition

As mentioned above, KGdP$_4$O$_{12}$ is a polymorphous compound. In addition to the $C2/c$ phase, it has two isothers, i.e. KGd(PO$_3$)$_4$ in $P2_1$ and $P2_1/n$. Both KGdP$_4$O$_{12}$ in $C2/c$ and KGd(PO$_3$)$_4$ in $P2_1/n$ can be prepared by crystallizing KH$_2$PO$_4$ and Gd$_3$O$_5$ from phosphoric acid below 550°C [27,28]. Because of the lower crystallization temperature and the resulting higher viscosity, it is difficult to grow bulk crystals of Nd:KGdP$_4$O$_{12}$. Parreau grew a KGd(PO$_3$)$_4$ crystal in $P2_1$ from a melt made from NH$_4$H$_2$PO$_4$, K$_2$CO$_3$ and Gd$_2$O$_3$ at a higher temperature [20]. In studying the crystallization region of KGd(PO$_3$)$_4$ ($P2_1$) in the ternary system Gd$_3$O$_5$–K$_2$O–P$_2$O$_5$, six neighbouring phases were found, and KGdP$_4$O$_{12}$ in $C2/c$ was one of them. By choosing the ratio in the melt composition, we successfully grew bulk crystals of Nd:KGdP$_4$O$_{12}$ (Figure 1(a)). The composition of a melt influences the formation of phase. A similar situation occurred to a Ba$_2$TeMo$_2$O$_9$ polymorphous compound recently reported—the α and β crystal phases can be grown from a melt with different compositions [29].

The chemical composition of the as-grown crystal was analyzed by ICP–AES (Table 1). The chemical formula of the crystal corresponds to KGd$_{0.99}$Nd$_{0.01}$P$_{0.01}$O$_{12}$, which is consistent with results of single crystal diffraction. The distribution coefficient of the neodymium ion at the structural sites of gadolinium ion is defined as $K_{Nd} = ([Nd]/([Nd]+[Gd]))_{crystal}/([Nd]/([Nd]+[Gd]))_{solution}$. This can be calculated from the data in Table 1 and the stoichiometry of the starting materials. The value (0.984) is very close to 1 because the ionic radius of Nd$^{3+}$ is only slightly bigger than that of Gd$^{3+}$. This means that the active Nd$^{3+}$ ion can be easily doped in the KGdP$_4$O$_{12}$ host crystal, and that the composition inside a single crystal would be homogeneous in general.

Table 1. The result of chemical analysis for the as-grown crystal of 5 at% Nd$^{3+}$-doped KGdP$_4$O$_{12}$.

| Element (mass%) | K (%) | Gd (%) | Nd (%) | P (%) |
|----------------|-------|--------|--------|-------|
| Calculated     | 7.64  | 29.20  | 1.38   | 24.22 |
| Experimental   | 7.27  | 28.98  | 1.38   | 23.86 |

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Figure 2. Structure projection of Nd:KGdP$_4$O$_{12}$ along the [010] direction. (Here, all the oxygen atoms have been omitted.).

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2. Crystal structure

Nd:KGdP\textsubscript{4}O\textsubscript{12} crystallizes in the monoclinic space group \(C2/c\) with cell parameters \(a = 7.812(2)\) Å, \(b = 12.307(3)\) Å, \(c = 10.474(2)\) Å, \(\beta = 110.84(3)^\circ\) and \(\zeta = 4\). Information regarding crystal data, data collection and refinement is given in Table S1. The atomic coordinate information is given in Table S2, and the anisotropic displacement parameter is given in Table S3. The lengths of P–O, Gd(Nd)–O and K–O bonds are listed in Table S4, and the bond valences have been calculated according to the Brown and Altermatt parameters [30] for the structure of Nd:KGdP\textsubscript{4}O\textsubscript{12}. The bond valence sums are reasonable for both cations and anions. The crystal structure of Nd:KGdP\textsubscript{4}O\textsubscript{12} we show here is consistent with that of undoped KGdP\textsubscript{4}O\textsubscript{12} reported by Ettis et al [27]. The Nd\textsuperscript{3+}-active ion occupies the lattice site of Gd\textsuperscript{3+}. The density of a single crystal of Nd:KGdP\textsubscript{4}O\textsubscript{12} at 23°C is 3.54 g cm\textsuperscript{-3}. This agrees well with the calculated value from the crystallographic data.

The basic structural unit of Nd:KGdP\textsubscript{4}O\textsubscript{12} is a centrosymmetric cyclotetraphosphate ring anion of \([\text{P}_4\text{O}_{12}]^{3-}\) that is composed of four PO\textsubscript{4} tetrahedra. Each PO\textsubscript{4} tetrahedron shares two corners (i.e. bridging oxygen) with the others. The four phosphorus atoms of each \([\text{P}_4\text{O}_{12}]^{3-}\) ring lie in the same plane due to symmetry, and all the oxygen atoms are either above or below the Pt plane. As shown in projection into the \(ac\) plane (Figure 2), the \([\text{P}_4\text{O}_{12}]^{3-}\) rings form layers parallel to \((001)\) at \(\zeta = 0\) and \(1/2\). A previous description [27] suggesting that these layers were perpendicular to the \([001]\) direction is erroneous because the normal of the \((001)\) faces is different from the \([001]\) direction. We note that the \([\text{P}_4\text{O}_{12}]^{3-}\) rings stack in the structure similar to fish scales. The Pt plane, i.e. (0.2908, −0.0415, 0.9559), is not parallel to \((001)\), and the interfacial angle between them is 17.08(2)^\circ.

The Gd(Nd)O\textsubscript{8} polyhedra and KO\textsubscript{10} polyhedra link the \([\text{P}_4\text{O}_{12}]^{3-}\) rings to form a three-dimensional framework. The eight vertexes of the Gd(Nd)O\textsubscript{8} polyhedra come from terminal oxygens of the PO\textsubscript{4} polyhedra, and they belong to six \([\text{P}_4\text{O}_{12}]^{3-}\) rings that are equal in the two adjacent layers. The Gd(Nd)O\textsubscript{8} polyhedra do not share any oxygen atoms and are isolated by the PO\textsubscript{4} and KO\textsubscript{10} polyhedra. Ettis et al [27] erroneously reported the shortest distance between the two rare earth ions to be 5.269 Å. Thus, they thought that it was small compared to the other alkali metal and rare earth tetraphosphates. Actually, the shortest Gd(Nd)–Gd(Nd) distance in the Nd:KGdP\textsubscript{4}O\textsubscript{12} crystal is 6.0059 Å, which is actually relatively long for tetraphosphates.

Figure S1 shows the experimental XRD pattern of the pulverized Nd:KGdP\textsubscript{4}O\textsubscript{12} crystal as well as our simulated pattern. The peak positions and diffraction intensities are consistent between the experimental and simulated XRD patterns. This confirms that our proposed structure is accurate.

For a laser crystal, the mechanical strength is due to the host material. Cleavage behaviour of the host crystal is related not only to the bond strength but also the geometry. There are three kinds of chemical bonds in potassium gadolinium phosphates: P–O, Gd–O and K–O. According to their covalent character, P–O bonds are much stronger than Gd–O and K–O bonds. The K–O bonds are the weakest of all. This is confirmed by the calculated results of bond valences shown in Table S5. The KGd(PO\textsubscript{3})\textsubscript{4} crystals have the strongest strength between the chains. In KGdP\textsubscript{4}O\textsubscript{12} however, the GdO\textsubscript{8} polyhedra and KO\textsubscript{10} polyhedra [\(\text{P}_4\text{O}_{12}\)]\textsuperscript{3-} rings to form a three-dimensional framework, and the strengths along the different directions are quite similar. Therefore, the Nd:KGdP\textsubscript{4}O\textsubscript{12} crystal does not have a prominent cleavage
behaviour. During the processing of Nd:KGdP4O12 crystals, no crack and cleavage as seen in KGd(PO3)4 crystals was found.

3. Crystal morphology and rocking curve
The as-grown crystal has some well-developed facets (Figure 1(a)) oriented using an XRD goniometer. The habit contains crystalline forms {hkl}, equivalent faces and corresponding the Bravais-Friedel and Donnay-Harker (BFDH) law. This established the theoretical morphological scheme of the Nd:KGdP4O12 crystal via the WinXMorph software [31] using the Bravais-Friedel and Donnay-Harker (BFDH) law. The morphological scheme is shown in Figure 1(b). Table 2 lists the crystalline forms {hkl}, equivalent faces and corresponding d_{hkl} for Nd:KGdP4O12.

While the as-grown crystal did not show a completely ideal morphology due to the restriction of the crystal growth method, all the predicted crystalline forms can be found on the as-grown single crystal. It should be noted that the {111} facet was smaller and limited by the growth conditions. Thus, it was quite pristine and we did not identify {111} for the as-grown crystal. The narrow tetragonal facet (021) on the as-grown crystal shows that {021} has a faster growth rate, which is consistent with the predicted scheme. The ideal morphology of KGdP4O12 is like a drum and hexagonal {001} facets reveal much more than other facets similar to drumheads. This relates to the structural feature of KGdP4O12 in which [P4O12]4− rings regularly array to form layers parallel to (001). The distance between the two [P4O12]4− rings adjacent to the two layers is larger than that from the same layer.

The rocking curve of the (004) diffraction plane of the as-grown Nd:KGdP4O12 crystal is presented in Figure S2. The diffraction peak is intense and with good symmetry without splitting, and its FWHM value is 0.006°. These results demonstrate that the as-grown Nd:KGdP4O12 crystal has a nearly perfect lattice structure.

4. IR and Raman spectra
The IR and Raman spectra of Nd:KGdP4O12 at room temperature are shown in Figure 3. The vibration frequencies above 600 cm−1 and their corresponding assignment are listed in Table S5 and are based on published findings [27,32]. In the low-frequency region below 600 cm−1, it is very difficult to distinguish the symmetric and antisymmetric bending modes of the O−P−O and P−O−P groups.

Compared to other cyclotetraphosphate compounds, we notice an absence of bands in the 750−1000 cm−1 region of the IR spectrum. This result is in agreement with the cyclic structure of Nd:KGdP4O12. The non-coincidence of the observed bands in the IR and Raman spectra indicates that the [P4O12]4− anion is centrosymmetric, which is in agreement with the above structural results.

A distinguishing characteristic also exits in the Raman spectrum. The symmetric stretching vibration of the P−O−P linkage−ν_s(P−O−P)−has a single peak at 684 cm−1. This is the strongest of all the Raman vibration peaks. However, for ν_s(P−O−P) of KGdPO4 [21], two peaks are observed in the range of 660−730 cm−1 and have the same intensity [24]. These are less than one half of the intensity of the ν_s(O−P−O). That is because of the symmetrical difference in the crystal structures and the different positions of the lanthanide and alkali ions. The obvious differences between the IR and Raman spectra of KGdP4O12 and KGdPO4 highlight how IR and Raman spectroscopy can identify the structure of alkali-metal lanthanide metaphosphates.

Table 3. The barycenter wavelength, experimental and calculated oscillator strengths, and absorption cross section of the Nd:KGdP4O12 crystal at room temperature.

| λ (nm) | 4f_{h/2}→J manifold | μ_ex (×10^{−6}) | μ_cal (×10^{−6}) | σ (×10^{−20} cm^2) |
|-------|---------------------|-----------------|-----------------|-----------------|
| 874   | 4F_{5/2}            | 2.04            | 2.04            | 0.68            |
| 802   | 4F_{5/2}+F_{7/2}    | 7.86            | 7.82            | 2.59            |
| 745   | 4F_{7/2}+S_{5/2}    | 8.75            | 8.79            | 3.09            |
| 683   | 4F_{5/2}            | 0.80            | 0.66            | 0.32            |
| 581   | 4G_{5/2}+G_{11/2}   | 11.46           | 11.46           | 2.25            |
| 520   | 2K_{13/2}+G_{7/2}+G_{9/2} | 4.98 | 5.00 | 0.79 |
| 470   | 2K_{13/2}+G_{9/2}+D_{15/2}+G_{11/2} | 1.34 | 1.26 | 0.26 |
| 431   | 2P_{1/2}            | 0.45            | 0.47            | 0.15            |
| 353   | 4D_{5/2}+D_{7/2}+F_{11/2}+D_{13/2} | 9.49 | 9.52 | 1.09 |

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Table 4. The calculated spontaneous emission probability, radiative branching ratios, radiative lifetime and experimental branching ratios of \( ^{4}F_{3/2} \) multiplet of Nd\(^{3+} \) in the Nd:KGdP\(_{4}\)O\(_{12} \) crystal.

| Transition | \( ^{4}F_{3/2} \rightarrow ^{4}I_{15/2} \) | \( ^{4}F_{3/2} \rightarrow ^{4}I_{11/2} \) | \( ^{4}F_{3/2} \rightarrow ^{4}I_{13/2} \) | \( ^{4}F_{3/2} \rightarrow ^{4}I_{15/2} \) |
|------------|----------------|----------------|----------------|----------------|
| \( A (s^{-1}) \) | 1112 | 1705 | 366 | 17 |
| \( I_{\text{max}} \) (%) | 34.8 | 53.3 | 11.4 | 0.5 |
| \( I_{\text{exp}} \) (%) | 28.6 | 58.8 | 12.6 | – |
| \( \tau (\times 10^{-6} \text{ s}) \) | 312 |

5. Thermal properties

Generally, double phosphate compounds are not stable at high temperatures. To measure the decomposition, a TG–DSC analysis for the Nd:KGdP\(_{4}\)O\(_{12} \) crystal was performed. The TG–DSC curves of the Nd:KGdP\(_{4}\)O\(_{12} \) crystal are given in Figure S3. A single sharp endothermic peak is observed at 920 \( ^{\circ} \text{C} \) from a crystalline phase, an amorphous phase was formed in the sample cell after the DSC measurement. The M\(^{11}\)\(\text{P}_{4}\)O\(_{12} \) compounds often decompose irreversibly into lanthanide tri-metaphosphates and alkali metal metaphosphates [33]. We thus conclude that the exothermic peak at 920 \( ^{\circ} \text{C} \) may be related to a decomposition of Nd:KGdP\(_{4}\)O\(_{12} \) in accordance with the reaction:

\[
\text{KGD}_{2}\text{O}_{12} (s) \rightarrow \text{GDP}_{3}\text{O}_{3}(s) + \text{KPO}_{3} (1)
\]

The decomposition temperature of the Nd:KGdP\(_{4}\)O\(_{12} \) crystal is much higher than that of KGd\(\text{PO}_{4}\)\(_{4} \) (\( P_{21} \) (878 \( ^{\circ} \text{C} \)) [20]. The difference in stability between these two potassium gadolinium metaphosphates can be explained by comparing their crystal data. The lengths of P–O bonds vary from 1.4752 to 1.6009 \( \text{Å} \) for KGd\(\text{PO}_{4}\)\(_{4} \). However, the P–O bond lengths vary from 1.4414 to 1.6886 \( \text{Å} \) for KGd\(\text{PO}_{4}\)\(_{4} \). That is, the PO\(_{4}\) tetrahedra in KGd\(\text{PO}_{4}\)\(_{4} \) are heavily distorted as are the GdO\(_{6}\) polyhedra. The Gd–Nd\(_{2}\)–O distances in the Nd:KGdP\(_{4}\)O\(_{12} \) are from 2.3665 to 2.4189 \( \text{Å} \) with an average of 2.3933 \( \text{Å} \). The Gd–O distances in KGd\(\text{PO}_{4}\)\(_{4} \) vary widely from 2.2903 to 2.4767 \( \text{Å} \) with an average of 2.4059 \( \text{Å} \). In addition, the volume per formula of KGd\(\text{PO}_{4}\)\(_{4} \) (235.3 \( \text{Å}^3 \)) is smaller than that of KGd\(\text{PO}_{4}\)\(_{4} \) (240.4 \( \text{Å}^3 \)). Thus, the thermal stability of the cyclic \( C_{2}/c \) space group should be better than that of the chain structure in the \( P_{21} \) space group.

For laser crystal materials, the damage threshold and possible laser applications can be greatly influenced by the specific heat. The specific heat is also an important value used to calculate thermal conductivity. Figure S4 shows that the constant pressure specific heat of the Nd:KGdP\(_{4}\)O\(_{12} \) crystal varies as a function of the temperature. The specific heat of the Nd:KGdP\(_{4}\)O\(_{12} \) crystal at room temperature (25 \( ^{\circ} \text{C} \)) is 0.521 J\(^{\circ} \text{C}^{-1} \text{g}^{-1} \). This is comparable to Nd:YAG (0.59 J\(^{\circ} \text{C}^{-1} \text{g}^{-1} \)) and Nd:YVO\(_{4} \) (0.51 J\(^{\circ} \text{C}^{-1} \text{g}^{-1} \)) [34]. Because Nd:YAG and Nd:YVO\(_{4} \) both have a high optical damage threshold, it follows that Nd:KGdP\(_{4}\)O\(_{12} \) should also have a high damage threshold [5]. The specific heat increases almost linearly from 0.485 to 0.799 J\(^{\circ} \text{C}^{-1} \text{g}^{-1} \) with temperature increases from –10 to 510 \( ^{\circ} \text{C} \). This suggests that the Nd:KGdP\(_{4}\)O\(_{12} \) crystal can tolerate even more thermal energy at a high temperature.

Figure 4 shows the thermal diffusivity and thermal conductivity of the Nd:KGdP\(_{4}\)O\(_{12} \) crystal. The thermal conductivity (\( \kappa \)) was calculated using the measured thermal diffusivity and specific heat according to \( \kappa = \rho C_{v} \), where \( \rho \) and \( C_{v} \) denote the thermal diffusivity, density and specific heat of the crystal at the same temperature, respectively. The thermal diffusivity of the crystal is 0.906 mm\(^2\)s\(^{-1}\) along the direction perpendicular to \( 001 \), i.e. the \( x \) direction, at 27.8 \( ^{\circ} \text{C} \). The calculated thermal conductivity of the crystal is 1.66 Wm\(^{-1}\)K\(^{-1}\) along the \( x \) direction correspondingly. This value is similar to that of Nd:SrLaGa\(_{3}\)O\(_{7} \) [4] and larger than those of some laser crystals with broad absorption such as NaLa\(_{3}\)(WO\(_{4}\))\(_{2} \) [2, 3] and Ca\(_{3}\)La\(_{2}\)(BO\(_{3}\))\(_{4} \) [5]. In laser designs, the thermal loading causes a temperature gradient in the crystal and leads to thermal expansion that results in thermal lensing and

Table 5. Comparison of spectroscopic properties of the Nd:KGdP\(_{4}\)O\(_{12} \) crystal with other Nd\(^{3+}\)-doped crystals.

| Crystal | Nd:KGdP\(_{4}\)O\(_{12} \) | Nd:SrLaGa\(_{3}\)O\(_{7} \) | Nd:KBaGd\(_{4}\)(MoO\(_{4}\))\(_{3} \) | Nd:YVO\(_{4} \) | Nd:YAG |
|---------|----------------|----------------|----------------|----------------|--------|
| Nd\(^{3+}\) (at%) | 5.0 | 1.0 | 0.91 | 1.0 | 1.0 |
| Crystal system | Monoclinic | Tetragonal | Monoclinic | Tetragonal | Cubic |
| Growth method | TSSG | Czochralski | TSSG | Czochralski | Czochralski |
| Peak absorption wavelength \( \lambda_{a} \) (nm) | 798 | 808 | 804 | 808.7 | 808 |
| FWHM at \( \lambda_{a} \) (nm) | 14.8 | 8 | 9 | 2 | 0.7 |
| Peak emission wavelength \( \lambda_{e} \) (nm) | 1057 | 1061 | 1069 | 1064 | 1064 |
| FWHM at \( \lambda_{e} \) (nm) | 14 | 14 | 24 | 1.1 | 0.8 |
| Fluorescence lifetime (\( \mu \text{s} \)) | 300 | 310 | 141 | 84 | 230 |
| Ref. | This work | [4] | [12] | [41] | [34] |

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other thermo-optic effects. All these effects would cause a decline in the quality of the laser beams and even crack the active crystal. The deposited heat would be easily transferred to the environment if the laser crystal possesses high thermal conductivity—this would minimize the thermal loading effects.

It is clearly shown in Figure 4 that the thermal diffusivity and thermal conductivity component of the Nd:KGdP4O12 crystal decreases with increasing temperature. Thermal conductivity is dominated primarily by its phonon thermal conductivity for the dielectric. This has two important determinants: the heat capacity and the phonon mean free path. Though the heat capacity of the Nd:KGdP4O12 crystal increases with temperature, the phonon-phonon scattering becomes much stronger and the phonon mean free path markedly decreases. Therefore, the final result is that the thermal conductivity decreases with temperature increases.

6. Absorption spectrum

Figure 5 shows the unpolarized absorption spectrum of the Nd:KGdP4O12 crystal at room temperature. The UV cut off is below 200 nm. This means that a large band gap would increase the damage resistivity of the crystal. All absorption lines are due to the 4f3–4f3 transition of the Nd3+ ions. Very strong absorption lines occur near 581, 747 and 798 nm, corresponding to the transitions of 4I13/2 → 2G5/2, 4I11/2, 4I13/2 → 2G5/2. In summary, the absorption lines of the Nd:KGdP4O12 crystal increases with temperature, the phonon-phonon scattering becomes much stronger and the phonon mean free path markedly decreases. Therefore, the final result is that the thermal conductivity decreases with temperature increases.

7. Fluorescence spectra analysis

The room temperature fluorescence spectrum of the Nd:KGdP4O12 crystal at 808 nm excitation was recorded from 330 to 1600 nm (Figure 6). Three emission bands corresponding to the 4F3/2 → 4I9/2, 4I11/2 and 4I13/2 transitions are observed at 860–920 nm, 1040–1080 nm and 1300–1380 nm, respectively. The room temperature emission FWHM of the transition 4F3/2 → 4I11/2 is 14 nm. This is evidence of the dominant contribution of inhomogeneous broadening to the spectra line-width in the low symmetry structure. The emission cross sections for the laser channel from 4F3/2 to 4I11/2 and 4I13/2 were calculated through the Fuchtbauer-Ladenburg (FL) formula [12,18]. These values are 1.11×10^-20, 6.25×10^-20 and 2.13×10^-20 cm^2, respectively.

The emission spectra of the Nd:KGdP4O12 at low temperature were studied to determine the Stark sublevels of the 4I13/2 and 4I11/2 excited multiplets and the ground state multiplet 4I9/2. Figure S3 shows the emission spectra of Nd:KGdP4O12 at 10K and 300K. These correspond to the transitions from 4F3/2 to 4I9/2, 4I11/2 and 4I13/2 levels, respectively. Figure 7 shows a schematic diagram of the Stark sublevels of Nd3+ in KGdP4O12 crystals obtained from the low temperature emission spectra. The 4F3/2 term is split into two components with ΔJ = 70 cm^-1. The low value of the crystal field splitting indicates that the crystal field of the KGdP4O12 host is weak. This is due to weak interactions between rare earth ions and oxygen atoms in contrast with the strong covalent bonds between P and O. In this regard, the Nd:KGdP4O12 crystal is similar to other double phosphates of alkali and lanthanide ions [38,39].

The fluorescence lifetime (τF) of the 4F3/2 energy level of Nd3+ in the Nd:KGdP4O12 crystal was determined to be 300 µs by fitting the decay curve exponentially (Figure S6). The long fluorescence lifetime would be beneficial to high energy storage during laser operation. Though the interatomic distance (6.0059 Å) between the nearest rare earth ions for KGdP4O12 is smaller than that for KGdPO4 [4] (6.5065 Å), it does not obviously affect the fluorescence lifetime. This is a function of the isolated GdO8 polyhedra in KGdP4O12. The τF of the Nd:KGd[PO4]3 crystal (92) is 244 µs with a very low doping concentration (0.6 at %) [38]. The values of NdLaP4O14 and NdNdP4O14 crystals are around 310 µs when doped with ~1 at % Nd3+ [40].

It is well known that the τF of Nd3+ ions generally decreases with increasing Nd3+ concentrations due to the interactions between the Nd3+ ions, i.e. the concentration quenching effect. However,
the Nd:KGdP4O12 crystal still has a long fluorescence lifetime of 300 μs under a higher doping concentration of 5 at%. Versus the above phosphates, the KGdP4O12 crystal is a distinct laser host material with a very low concentration quenching for Nd3+ because the Nd:KGdP4O12 crystal ensures a long fluorescence lifetime even under a high active ion concentration.

The calculated τf of the 4F9/2 energy level is 312 μs (Table 4). Thus, the fluorescent quantum efficiency (η = τf/τo) of the 4F9/2 level is 96%. For solid-state laser materials, low crystal field strength leads to weak electron-phonon interactions and further leads to high quantum efficiency. The previous data describing weak Stark splitting of the Nd flirt energies levels further supports the calculated result showing that Nd:KGdP4O12 has a high quantum efficiency.

Some spectroscopic properties of the Nd:KGdP4O12 crystal are listed in Table 5 as well as those of other Nd3+-doped crystals including YAG and YVO4 crystals with ordered structures and SrLaGa3O7 and KBaGd(MoO4)3 crystals with disordered structures. The FWHM value of Nd:KGdP4O12 at λs is not only much larger than those of Nd:YAG and Nd:YVO4 crystals, but also larger than those of Nd:SrLaGa3O7 and Nd:KBaGd(MoO4)3 crystals. This suggests that the Nd:KGdP4O12 crystal can be pumped more effectively by AlGaAs laser diode, but not be restricted to the temperature stability of the output wavelength in the laser diode. The quality factor (M) of a laser material is proportional to its doping concentration (M) and fluorescence lifetime (τf). A high value of M generally means a low oscillation threshold in subsequent laser operations. Therefore, the high doping concentration and long fluorescence lifetime of Nd:KGdP4O12 makes it possible to achieve a continuous wave laser action. In addition, Nd:KGdP4O12 can be used as a tunable laser material with a very broad emission band near 1060 nm.

Conclusions

We successfully grew a macro-defect-free single crystal of 5 at% Nd3+-doped KGdP4O12 with very good crystallinity using TSSG−SC from self-flux. To the best of our knowledge, both the growth of the bulk crystals and doping with neodymium are shown here for the first time in KGdP4O12. The Nd:KGdP4O12 crystallizes in space group C2/c, and the phosphoric anions have a cyclic geometry of [P4O12]6−. The crystal has good chemical stability and does not show cleavage like its isomer KGd(PO3)4. The distribution coefficient of neodymium ion is very close to 1, so gadolinium ion can be evenly substituted. The absorption and fluorescence spectra of the Nd:KGdP4O12 crystal were investigated at room temperature. The peak absorption cross section at 798 nm is 2.59×10−20 cm2 with a FWHM of 14.8 nm. Such a broad FWHM in the absorption band is suitable for InGaAs laser diode pumping. The radiation and fluorescence lifetimes of the excited state 4F9/2 are 312 and 300 ms, respectively. These result in a high luminescent quantum efficiency of 96%. The emission from the 4F9/2 energy level to the 4I11/2 manifold is more feasible than that of the 4I5/2 manifold. The peak emission cross section at 1057 nm (corresponding to 4F9/2→4I11/2) is 6.25×10−20 cm2. In addition, the KGdP4O12 crystal presents positive thermal characteristics. It has a good thermal stability with decomposition at 920°C. At room temperature, the specific heat and the thermal conductivity along the c axis are 0.521 Jg−1K−1 and 1.66 Wm−1K−1, respectively. In summary, the Nd:KGdP4O12 crystal may be regarded as a potential solid-state laser material for laser diode pumping.

Supporting Information

Figure S1 The experimental XRD pattern of Nd:KGdP4O12 from polycrystalline powder and the simulated pattern from single crystal data.

Figure S2 XRD rocking curve of the (004) diffraction plane of the as-grown Nd:KGdP4O12 single crystal.

Figure S3 TG and DSC curves of the Nd:KGdP4O12 crystal.

Figure S4 Specific heat versus temperature curve of the Nd:KGdP4O12 crystal.

Figure S5 Emission fluorescence spectra of the Nd:KGdP4O12 crystal at 10K and 300K.

Figure S6 Fluorescence decay curve of the 4F9/2 manifold of the Nd:KGdP4O12 crystal at room temperature.

Table S1 Crystal data, data collection and refinement of Nd:KGdP4O12.

Table S2 Atomic coordinates and equivalent isotropic displacement parameters of Nd:KGdP4O12.

Table S3 Anisotropic displacement parameters (Å2) of Nd:KGdP4O12.

Table S4 Bond lengths and bond valences in the Nd:KGdP4O12 crystal.

Table S5 Frequencies (cm−1) and assignments of IR absorption and Raman scattering for Nd:KGdP4O12.
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Author Contributions

Conceived and designed the experiments: TS YK JX. Performed the experiments: TS YZ. Analyzed the data: TS YZ PS ZZ. Contributed reagents/materials/analysis tools: TS SC. Wrote the paper: TS.

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