

Growth, anisotropic spectroscopy and laser operation of the monoclinic Nd:KGd(PO₃)₄ crystal

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Abstract

Type III KGd(PO₃)₄ and Nd:KGd(PO₃)₄ single crystals have been successfully grown. We have proved that these crystals have a wide transparency window closing at 160 nm in the UV region and extending to 4 μm in the IR region. We have determined that a slight rotation occurred for the dielectric frame in the 355-1064 nm range of wavelengths. We have measured the absorption in the ⁴I_{9/2} → ⁴F_{5/2} channel and the emission in the ⁴F_{3/2} → ⁴I_{11/2} channel. In addition to the three *N_p*, *N_m*, *N_g* usual polarizations, a fourth spectroscopic parameter was needed for a full description. Lasing was obtained at 1052.4 nm in *N_p* polarization (ordinary wave) for propagation in the *N_g*-*N_m* principal plane.

Keywords: Laser materials, Nonlinear optical materials, Absorption, Emission

1. Introduction

Solid state lasers in the visible and the ultraviolet range are interesting for many applications such as high density optical data storage and medicine, among others [1-5]. The use of nonlinear optical materials (NLO) allows frequency conversion of the infrared radiation emitted by many rare-earth ions to obtain visible or ultraviolet radiation depending on the fundamental radiation and mainly on the harmonic order. Type III KGd(PO₃)₄ (hereafter KGdP) is an attractive NLO material for laser host of active rare earth ions. It is a monoclinic crystal that crystallizes in the *P*2₁ space group [6] with unit cell parameters *a* = 7.2701(11), *b* = 8.3818(8), and *c* = 7.9608(10) Å, *β* = 91.776(12)°, *Z* = 2, and *V* = 484.87(11) Å³. Its noncentrosymmetry allows it to have second harmonic generation (SHG) efficiency comparable to KH₂PO₄ (KDP) [6]. It can be easily doped with different lanthanide elements, like Nd or Yb substituting Gd with the possibility to obtain second harmonic of the radiation emitted by the lanthanide ions present in the same doped crystal (self-doubling material in the case of SHG). The substitution of part of Gd for Nd in the KGdP structure has the advantage that KGdP and KNd(PO₃)₄ (KNP) crystallize in the same space group, while KYb(PO₃)₄ (KYbP) crystallizes in another monoclinic space group. Thus, substitution with Nd is possible up to 100 % by maintaining the same crystalline phase, while in the case of Yb, the crystalline phase is maintained only for partial substitution [7,8].

In addition, KGdP exhibits a broad transmission window, closing at 160 nm in the UV region (1/e of the maximum value at 165 nm) and extends to 4 μm in the IR region. It is a deep-ultraviolet NLO material, since is transparent in the region with wavelengths below 200 nm. Only a few materials are transparent in this region and they are mainly borates as KBe₂BO₃F₂ (KBBF) [9,10], β-BaB₂O₄ (BBO) [11,12], K₃B₆O₁₀Cl [13,14],

LiB_3O_5 (LBO) [15], $\text{CsLiB}_6\text{O}_{10}$ (CLBO) [16], $\text{K}_2\text{Al}_2\text{B}_2\text{O}_7$ (KABO) [17], $\text{Na}_2\text{Be}_4\text{B}_4\text{O}_{11}$ [18], $\text{LiNa}_5\text{Be}_{12}\text{B}_{12}\text{O}_{33}$ [18] and $\text{Li}_4\text{Sr}(\text{BO}_3)_2$ [19], although recently it has been demonstrated that $\text{RbBa}_2(\text{PO}_3)_5$ has a transparency window closing at 163 nm [20]. Table 1 shows the comparison of the UV and IR absorption edges of different NLO crystals.

Table 1. UV and IR absorption edges for different NLO crystals.

Crystal	UV absorption edge (nm)	IR absorption edge (nm)	Reference
KGdP	160	4000	This work
KBBF	153	3780	[10, 22]
BBO	189	3500	[22]
KABO	180	3600	[22]
CLBO	175	2750	[22]
$\text{K}_3\text{B}_6\text{O}_{10}\text{Cl}$	180	3460	[14]
$\text{Na}_2\text{Be}_4\text{B}_4\text{O}_{11}$	169	-	[18]
$\text{LiNa}_5\text{Be}_{12}\text{B}_{12}\text{O}_{33}$	171	-	[18]
$\text{Li}_4\text{Sr}(\text{BO}_3)_2$	186	-	[19]
LBO	155	3200	[15, 21]
$\text{RbBa}_2(\text{PO}_3)_5$	163	-	[20]

The wide transparency window of KGdP makes this crystal candidate for obtaining visible and ultraviolet radiation by using harmonic conversion of the radiation emitted by different lanthanides [6,8]. An important advantage of KGdP with respect to other deep-ultraviolet NLO crystals is that Gd can be easily substituted by other lanthanides and in the same crystal is possible to obtain laser radiation and doubling the frequency of these radiation, that is to say, a self-doubling crystal. Another interesting application of this crystal to take advantage of the low cut-off wavelength in the UV region is for angle-resolved photoemission spectroscopy (ARPES), a powerful tool in probing the electronic structure of solids [10]. On the other hand, these crystals could be used as scintillators by doping them with lanthanides with absorption peaks at low wavelengths (ionizing radiation) and emission in the visible range [23].

The hardness of KGdP is close to that of quartz in the Moh's scale, which allows polishing the samples with high optical quality [24]. Its almost isotropic thermal expansion is an advantage for processing the laser elements and during laser action.

Efficient 1 μm laser operation in Yb doped KGdP was achieved by Parreu *et al.* in 2007 [25]. The output power obtained was low, of the order of 100 mW, due to the small size of the crystal used and the doping level, but the slope efficiency was enough high, with a value of 55 %.

A key-point is that for monoclinic or triclinic symmetries, absorption and fluorescence extrema do not coincide with the three principal X, Y, Z axes of the dielectric frame. So the three usual spectroscopic X, Y, Z polarization measurements are not sufficient for a full description of the whole spatial distribution. In the field of laser materials, only recently a few authors devoted efforts to this aspect: first with the monoclinic $\text{Nd}^{3+}:\text{YCa}_4\text{O}(\text{BO}_3)_3$ [26, 27], then with $\text{Nd}^{3+}:\text{La}_2\text{CaB}_{10}\text{O}_{19}$ [28] and $\text{Yb}^{3+}:\text{La}_2\text{CaB}_{10}\text{O}_{19}$ [29]. We report here this topic in the case of the Nd:KGdP crystal with a special attention to the wavelength dependence of the anisotropy.

The present paper includes the description of the results of the crystal growth, a detailed study of the transparency range and the first laser operation of neodymium in this family of compounds.

2. Single crystal growth

KGdP melts incongruently at 1142 K [30] and consequently it can not be grown directly from the melt of its stoichiometric composition. Thus, KGdP and Nd:KGdP single crystals have been grown from self-flux solutions, without the presence of foreign ions that can be introduced in the crystalline structure. The technique used to grow these crystals was Top Seeded Solution Growth (TSSG) and the supersaturation of the solution was obtained by slowly cooling of the solution [31].

The solutions were prepared in cylindrical 125 cm³ platinum crucibles and the solution weight was about 130 g. The reagents used were K₂CO₃ (99.9 % from Fluka), Gd₂O₃ (99.9 % from Sigma Aldrich) and NH₄H₂PO₄ (99.9 % from Fluka) and Nd₂O₃ (99.9 % from Fluka) for doping.

Previously to this work, we determined the crystallization region of KGdP in self-flux solutions [30]. From these results, we choose suitable solutions for single crystal growth, with composition K₂O : (1-x) Gd₂O₃ + x Nd₂O₃ : P₂O₅ = 34 : 6 : 60 (mol ratio) with x ranging from 0 to 0.005. Some physical properties of these solutions, important for crystal growth, such as density, surface tension and dynamic viscosity have been measured as a function of the temperature. Near to the saturation temperature (950 K) the density of the undoped solution is 2.38 x 10³ kg/m³, the surface tension has a value of 137.5 x 10⁻³ N/m and the dynamic viscosity is 19 Pa.s [32]. Due to the high level of dynamic viscosity of this solution, we used a platinum stirrer (diameter 1.8 cm) rotating at 70 rpm with change of rotation direction every 50 seconds, in order to produce a forced convection in the solution to help in its homogenization [24].

The KGdP seed was located at the surface of the solution, at 1.2 cm from the center and rotated through the same axis and with the same angular velocity as the stirrer. In all the crystal growth experiments, the seed was orientated with the **a*** crystallographic direction perpendicular to the surface of the solution because, in a previous work, it has been proved that this orientation give good results in single crystal growth experiments [24].

Because of the high dynamic viscosity of the solution and in order to favors the natural convection, an axial thermal gradient of 14 K/cm in the solution was applied. The radial thermal gradient was 6 K/cm.

The saturation temperature of the solution was measured by repeated measurement of the growth/dissolution rates at different temperatures using a KGdP seed. Once determined this temperature, the solution was cooled at a rate of 0.1 K/h for 15 K and 0.05 K/h for the next 9-15 K in order to obtain the necessary supersaturation for the crystal growth. During all the crystal growth process, the platinum stirrer had a rotation of 70 rpm, with change of rotation every 50 s. Once the thermal ramp was finished, the crystal was removed slowly from the solution and maintained slightly above the surface of the solution, while the furnace was cooled to room temperature at a rate of 25 K/h.

The single crystals obtained were transparent and generally free of inclusions and cracks. As an example, Figure 1(a) shows an as-grown Nd:KGdP single crystal and figure 1(b) shows a crystal scheme with the faces observed in the crystal made with the Shape program.

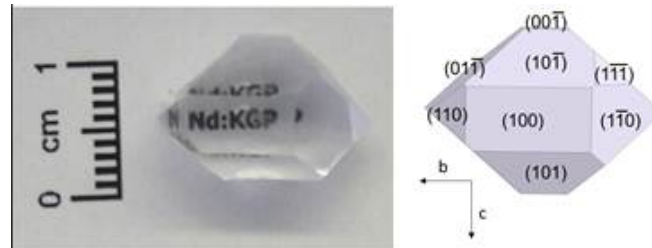


Figure 1. (a) As-grown single crystal of KGdP; (b) crystal scheme with the crystal the faces observed.

Table 2 shows the growth conditions and the dimensions, weight and growth rate of the single crystals obtained for different growth experiments. The weight of the crystals ranged from 2.56 to 4.33 g and their dimensions ranged from 9.1 to 11.4 mm along **a*** direction, from 15.6 to 19.5 mm along **b** direction and from 9.2 to 13.5 mm along **c*** direction. In all the crystals obtained, the crystal dimension along **b** direction is higher than the dimensions along **a*** and **c*** directions. These two last dimensions are similar in the main part of the crystals.

Table 2. Crystal growth conditions and crystals obtained.

Experiment number	[Nd ₂ O ₃]/([Gd ₂ O ₃]+[Nd ₂ O ₃]) (mol %) in the solution	Cooling rate (K/h)	Cooling interval (K)	Crystal weight (g)	Crystal dimensions along a* x b x c* directions (in mm)	Growth rate (x 10 ⁻³ g/h)
1	0	0.1 0.05	15 9	2.56	10.5x15.7x9.2	7.76
2	0	0.1 0.05	15 15	4.33	11.4x18.8x10.6	9.62
3	0	0.1 0.05	15 9	4.30	10.5x19.5x13.5	13.03
4	0.5	0.1 0.05	15 9	2.60	9.3x15.6x10.5	7.88
5	0.5	0.1 0.05	15 15	3.28	9.7x17.1x12.8	7.29
6	0.5	0.1 0.05	15 10	2.58	9.1x15.7x10.7	7.37

The Nd contents in the crystals was measured by electron probe microanalysis (EPMA) with wavelength dispersive spectroscopy (WDS), using a Cameca SX 50 equipment. For the K, Gd, P and O measurements, an undoped KGdP single crystal was used as standard, while for the Nd measurement, the standard used was REE4. The K_{α} lines of K, P and O and the L_{α} lines of Nd and Gd with a beam current of 10 nA and an accelerating voltage of 20 KV were used for the measurements.

From these data, we calculated the distribution coefficient of Nd when part of Gd₂O₃ was substituted by Nd₂O₃ in the solution, according to the expression:

$$K_{Nd} = ([Nd]/([Nd] + [Gd]))_{crystal} / ([Nd]/([Nd] + [Gd]))_{solution}$$

When 0.5 mol % of Gd₂O₃ was substituted by Nd₂O₃ in the solution, the crystal composition was KGd_{0.993}Nd_{0.007}(PO₃)₄, which means 0.288×10^{20} Nd³⁺ at/cm³ in the crystal. The distribution coefficient of Nd³⁺ in KGdP was slightly higher than unity, $K_{Nd} = 1.38$.

These crystals were cut with a diamond saw along the principal optical directions N_g , N_m and N_p and along the **a***, **b** and **c** crystallographic directions to obtain cubes with dimensions about $5 \times 5 \times 5$ mm³ and polished with diamond powder up to 0.1 μm. These samples were used for the spectroscopic measurements.

3. Transparency window of KGd(PO₃)₄

It is important for both research and device engineering to measure accurately the optical transmission window of the material. We recorded the transmission spectra of a KGdP sample cut as slab and polished to optical quality and with their input and output faces oriented perpendicularly to the **b** axis. The measurements of the transparency window of KGdP were carried out between 120 nm and 3.0 μm by using a Cary 500 spectrophotometer and between 2.5 and 9.0 μm by using a Midac Prospect Fourier-Transform IR (FTIR) spectrometer at room temperature, using unpolarized light in both cases. In the UV and IR regions, spectra were recorded in N₂ atmosphere, avoiding absorptions of oxygen and water vapor, respectively, present in the air.

As can be seen in figure 2, KGd(PO₃)₄ presents a wide transparency window that extends from 165 nm to practically 4 μm. We defined the limits of this optical transparency window when the maximum value of transmittance decreased by a factor 1/e in the UV and IR regions. The UV edge at zero transmission is 160 nm.

The fact that the optical transparency window is closed at so short wavelengths in the UV region implies the existence of a wide band gap in this region of the electromagnetic spectrum for this material [33]. Having a so wide band gap, this crystal is expected to present a high resistance to optical damage [34]. Furthermore, apart from the potential use of this crystal as a crystalline matrix for laser active ions, such as Ce³⁺, emitting in the UV region of the spectra [35], and taking into account that this crystal is a non-linear optical crystal, [6] it can be used as a suitable material to generate high order

harmonics, such as the 3rd and the 4th harmonics of Nd:YAG lasers. Thus, this transparency window also covers the range of wavelengths at which the Nd³⁺ ion absorbs and emits radiation. In addition, due to the extension of the transparency window of this crystal to very short wavelengths, it could be used for angle-resolved photoemission spectroscopy (ARPES) as KBe₂BO₃F₂ (KBBF), with the advantage that KGdP can be grown with tabular shape, while it is difficult to grow KBBF crystals thicker than 1 mm [10]. By doping KGdP with Ce³⁺, Pr³⁺ or other active ions with absorption at low wavelengths and emission at higher wavelengths, this crystal could be used as scintillator [23].

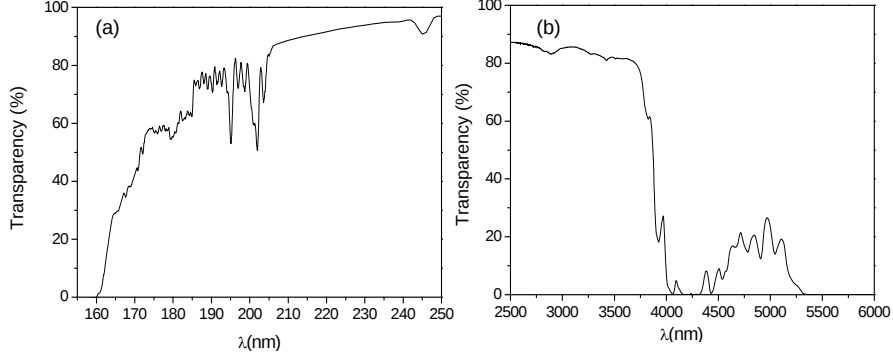


Figure 2. Limits of the transparency window of KGd(PO₃)₄ at room temperature in (a) the UV region and (b) in the IR region.

As can be seen in figure 2, there are two absorption peaks located at 195 and 202 nm which can be associated to the Gd transitions $^8S_{7/2} \rightarrow ^6G_{13/2}$ and $^8S_{7/2} \rightarrow ^6G_{7/2}$, respectively. The existence of optical absorption bands in the UV region of the electromagnetic spectrum, close to the limit of the transparency window in this region, can affect the optical transparency of the crystal. These bands, in several occasions, are associated to an increase of the optical damage that can be enhanced when doping the crystal with ions that absorb in this region.

The limit of the transparency window in the IR region is due to the phosphate groups in the crystals, and is related with the first and second overtones of the ν_3 and ν_1 vibrations of the P-O bonds in the tetrahedrons of PO₄ [36].

4. Optical spectroscopy of Nd³⁺ in the monoclinic KGd(PO₃)₄

4.1. Theoretical background

The two-fold **b** crystallographic axis of the KGdP crystal coincides with the $N_p=X$ ($=b$) principal axis of the dielectric frame. The two other $N_m=Y$ and $N_g=Z$ principal axes lie in the **a-c** crystallographic plane with an orientation determined in the next 4.2 section (Positive biaxial crystal with $n_z > n_y > n_x$)

The imaginary symmetric part ϵ'' (describing absorption or amplification) of the permittivity tensor is diagonal in a X', Y', Z' frame deduced by a θ_0 -rotation from the X, Y, Z frame around the X ($=b$)= X' axis as it is allowed by the monoclinic symmetry. The consequence is that generally the polarization for achieving the absorption and fluorescence extrema does not coincide with the polarization along the three principal X, Y, Z axes. A nondiagonal term ϵ''_{yz} appears if we express ϵ''_{ij} in the XYZ frame from its diagonal expression $\epsilon''_{i'j'}$ in the $X'Y'Z'$ frame:

$$\begin{bmatrix} \epsilon''_{xx} & 0 & 0 \\ 0 & \epsilon''_{yy} & \epsilon''_{yz} \\ 0 & \epsilon''_{yz} & \epsilon''_{zz} \end{bmatrix} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & \cos \theta_0 & \sin \theta_0 \\ 0 & -\sin \theta_0 & \cos \theta_0 \end{bmatrix} X \begin{bmatrix} \epsilon''_{x'x'} & 0 & 0 \\ 0 & \epsilon''_{y'y'} & 0 \\ 0 & 0 & \epsilon''_{z'z'} \end{bmatrix} X \begin{bmatrix} 1 & 0 & 0 \\ 0 & \cos \theta_0 & -\sin \theta_0 \\ 0 & \sin \theta_0 & \cos \theta_0 \end{bmatrix} \quad (1)$$

where the absorption or amplification coefficient is:

$$k_i = N \sigma_i = \frac{2\pi}{n_i \lambda} \mathcal{E}''_{ii} \quad (2)$$

N being the involved population and σ_i the cross-section.

Inspection of $\mathcal{E}''_{ij}$ reveals that the θ_0 angle can be obtained from the expression:

$$\tan(2\theta_0) = \frac{2\mathcal{E}''_{yz}}{\mathcal{E}''_{zz} - \mathcal{E}''_{yy}} \quad (3)$$

The propagation modes result from the Fresnel equation which is the characteristic equation of a 2-dimension eigenvalue problem whose exact solutions [29, 37] can be simplified because the imaginary part is much weaker than the real one. Then the θ -polar angle dependence of the absorption coefficient $k(\theta, \lambda)$ in extraordinary polarization for propagation in the $N_m=Y - N_g=Z$ principal plane is described with the formula:

$$\frac{k(\theta, \lambda)}{n_e^3(\theta, \lambda)} = \frac{k_y(\lambda)}{n_y^3(\lambda)} \cos^2(\theta) + \frac{k_z(\lambda)}{n_z^3(\lambda)} \sin^2(\theta) - \frac{4\pi}{\lambda} \frac{\mathcal{E}''_{yz}(\lambda)}{n_y^2(\lambda) n_z^2(\lambda)} \sin(\theta) \cos(\theta) \quad (4)$$

whereas the fluorescence intensity $I(\theta, \lambda)$ is obtained [29] with the replacement

$$k = \frac{\lambda^4}{n^2} I :$$

$$\frac{I(\theta, \lambda)}{n_e^5(\theta, \lambda)} = \frac{I_y(\lambda)}{n_y^5(\lambda)} \cos^2(\theta) + \frac{I_z(\lambda)}{n_z^5(\lambda)} \sin^2(\theta) - \frac{4\pi}{\lambda^5} \frac{\mathcal{E}''_{yz}(\lambda)}{n_y^2(\lambda) n_z^2(\lambda)} \sin(\theta) \cos(\theta) \quad (5)$$

Three adjustable parameters for each wavelength: $k_y(\lambda)$, $k_z(\lambda)$ and $\mathcal{E}''_{yz}(\lambda)$ (and similarly for the emission described below in section 4.4: $I_y(\lambda)$, $I_z(\lambda)$ and $\mathcal{E}''_{yz}(\lambda)$) allow the fitting of as much as possible experimental absorption (emission) spectra recorded in different θ - directions. The spectrum in $N_p=X$ ordinary polarization and propagation in the principal plane has no θ - dependence.

The set of parameters $(\theta_0, \mathcal{E}''_{y'y'}, \mathcal{E}''_{z'z'})$ involved in expression (1) is not unique, the $\mathcal{E}''_{ij}$ tensor expressed in the dielectric frame, the $\tan(2\theta_0)$ and the spectroscopy description are unchanged under the transformation $(\theta_0, \mathcal{E}''_{y'y'}, \mathcal{E}''_{z'z'}) \rightarrow (\theta_0 + \pi/2, \mathcal{E}''_{z'z'}, \mathcal{E}''_{y'y'})$.

Finally let us specify that the θ_0 -rotation is $\pm \frac{\pi}{4}$ if the denominator in equation (3)

vanishes. It can occur at a few wavelengths and in any case these wavelengths should be close to the ones at which the two $k_y(\lambda)$ and $k_z(\lambda)$ spectra are equal because the refractive indices in equation (2) are numerically not so different (within about 1%). This is a peculiar case of the following approximation. Equations (4) and (5) have no rigorous symmetry but it can be used the approximated θ -dependence obtained neglecting the refractive index differences. With the help of expression (1) the approximated θ -dependence written in the absorption case is:

$$k(\theta, \lambda) = \frac{2\pi}{\lambda n_e} \left(\mathcal{E}''_{y'y'}(\lambda) \cos^2(\theta - \theta_0) + \mathcal{E}''_{z'z'}(\lambda) \sin^2(\theta - \theta_0) \right) \quad (6)$$

where n_e is the average of the extraordinary refractive index. Expression (6) has evident symmetry properties in relation to the θ_0 -direction ($=X'$ axis) and $(\theta_0 + \pi/2)$ -direction ($=Y'$ axis). If two spectra recorded in two different θ -directions of propagation are equal at a

given wavelength, this means that these two directions have the θ_0 -direction (and the $(\theta_0+\pi/2)$ -direction) as their bisectrix according to the symmetry of equation (6) approximation and close to the bisectrix according to the rigorous equation (4) or (5).

4.2. Orientation of the dielectric frame

This section is devoted to the linear optical properties due to the real part of the permittivity. After the refractive indices of KGdP were been measured by Parreu et al. [25], no wavelength dependence of the N_m - N_g principal axes has been reported in literature. The known value is clockwise 37.3° for the c - N_g angle at 633 nm when positive b is pointed to the observer. However the monoclinic symmetry allows a rotation of the dielectric frame around the $b=N_p$ two-fold axis by changing the wavelength which can be quite important. This is for example the case of the bismuth borate BiB_3O_6 where more than 3° rotation is observed in the 365-1000 nm range of wavelengths [38] and more recently a systematic study has been performed by Traum et al. [39] for other monoclinic optical crystals.

The N_p -face of a Nd:KGdP sample was polished and carefully aligned with the beams of several lasers: a frequency tripled Nd:YAG laser at 355 nm, a collimated laser diode at 405 nm, a solid-state laser at 532 nm, a helium-neon laser at 633 nm and a YAG:Nd laser at 1064 nm. The sample was located between two crossed polarizers. The emergent beam was detected with a Si detector from Edmund Optics connected to a Keitley μ volt-meter. The angular position of the beam extinction due to the sample rotation was accurately determined by fitting a larger number of detected signals at different angular positions. The rotation stage is graduated every 1.7 arcmin leading to an error of ± 0.85 arcmin. .

The rotation of the N_m - N_g principal axes around the $N_p=b$ axis versus the wavelength is represented in figure 3. We can see that the angle between the N_g direction and c direction increases drastically in the UV spectral domain. The inset in figure 3 gives, for comparison, the angular positions of the dielectric frame axes at 633 nm.

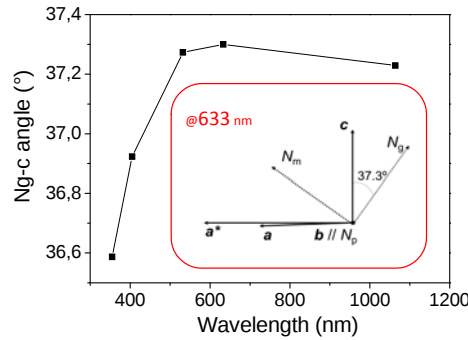


Figure 3. Rotation versus wavelength of the N_m - N_g principal axes around the $N_p=b$ axis. The inset shows some useful directions, the $N_p=b$ with positive axis pointing to the reader.

4.3. Optical absorption

Optical absorption measurements were made using a Cary 500 spectrophotometer at room temperature (300 K). A Polarizer Glan–Taylor Prism was used to perform the absorption measurements with light polarized parallel to the principal optical directions of the samples.

When the KGdP structure is doped with Nd^{3+} , these ions substitute the Gd^{3+} ions and they are located in a unique site with C_1 symmetry. Since Nd^{3+} has an odd number of electrons in the 4f shell (Nd^{3+} electronic configuration: $[\text{Xe}]4f^3$), selection rules depending on the polarization of the light are not expected, although the intensity of the individual peaks may vary due to differences in refractive indices with the direction of polarization of the light.

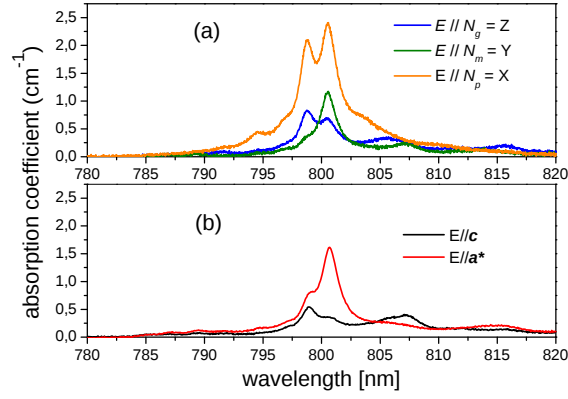


Figure 4. Absorption coefficients for ≈ 0.5 at % $\text{KGd}(\text{PO}_3)_4$ with light polarized parallel to (a) N_p , N_m , N_g polarizations; (b) parallel to a^* and c directions.

Figure 4(a) shows the polarized optical absorption coefficient of Nd^{3+} in KGdP in the wavelength range between 780 and 820 nm with polarization along the three principal optical axes. In this figure it can be observed the electronic transition from the ground state to the excited manifolds $^4F_{5/2} + ^2H_{9/2}$ and this region is also of interest for readily available diode pump laser sources. As it was expected, the anisotropy of the optical absorption was significant and the absorption coefficient was maximized for $E // N_p$ with a maximum value 2.43 cm^{-1} at 800.6 nm (12500 cm^{-1}), measured with the Nd^{3+} concentration of $0.288 \times 10^{20} \text{ cm}^{-3}$. At the same wavelength, the optical absorption coefficient for $E // N_m$ is 1.16 cm^{-1} and for $E // N_g$ is 0.69 cm^{-1} . Figure 4(b) shows the optical absorption coefficient of Nd^{3+} in KGdP with polarization along a^* and c measured in a second $\text{Nd}^{3+}:\text{KGdP}$ sample.

Figure 4(b) shows the optical absorption coefficient of Nd^{3+} in KGdP for the same electronic transition with polarization parallel to a^* (propagation along c) and to c (propagation along a^*) directions measured in a second $\text{Nd}^{3+}:\text{KGdP}$ sample, being the values 1.61 cm^{-1} and 0.35 cm^{-1} , respectively.

Then, the maximum absorption cross section is for $E // N_p$, and in this case the values is around $8.4 \times 10^{-20} \text{ cm}^2$. This value is larger than the ones reported for other well-known hosts for self-frequency doubling of Nd, such as $\text{LiNbO}_3:\text{MgO}$, $\text{YCa}_4\text{O}(\text{BO}_3)_4$ (YCOB) and $\text{YAl}_3(\text{BO}_3)_4$ (YAB), which values are 2.7×10^{-20} , 1.4×10^{-20} and $2.58 \times 10^{-20} \text{ cm}^2$, respectively [40,41].

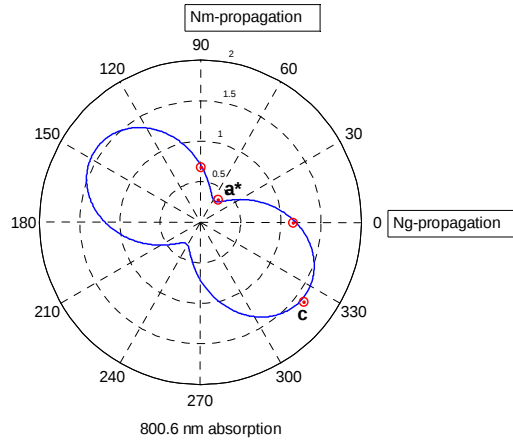


Figure 5. Full angular distribution of the absorption coefficient at 800.6 nm for propagation in the N_m - N_g principal plane in extraordinary polarization.

Considering the optical absorption coefficients at 800.6 nm, the full angular distribution in the XZ principal plane of the extraordinary mode at this wavelength, calculated with equation (4), is shown in figure 5. We have used the four experimental absorption spectra recorded in $Y=N_m$, $Z=N_g$, $\mathbf{a}^*$ and $\mathbf{c}$ -polarizations, with propagation directions Z , Y , $\mathbf{c}$ and $\mathbf{a}^*$, respectively. As said before, the spectrum in $N_p=X$ ordinary polarization and propagation in the principal plane has no θ -dependence. The angular distribution is obtained adjusting three parameters: k_y (at 800.6 nm), k_z (at 800.6 nm) and $\mathcal{E}_{yz}''$ (at 800.6 nm), the four experimental data being represented by the red circles. We can see that the absorption extrema do not coincide with the propagation along the Y and Z principal axes. However, for the maximum absorption of neodymium for this transition at 800.6 nm, the θ angle corresponds to almost 35° , and this would be almost coincident with the propagation along $\mathbf{c}$ and $E//\mathbf{a}^*$. A similar rotation has been observed for this neodymium transition in YCOB, in which the rotation of the optical absorption main axis in relation with the dielectric axis was around 31° [42].

Such fitting can be performed for each wavelength. The obtained $\mathcal{E}_{yz}''(\lambda)$ parameter, which is the fourth spectroscopic parameter specific to the monoclinic symmetry, is provided in figure 6(a). The equivalent θ_0 -rotation of the $Y'Z'$ frame is visualized versus the absorption wavelength in figure 6(b).

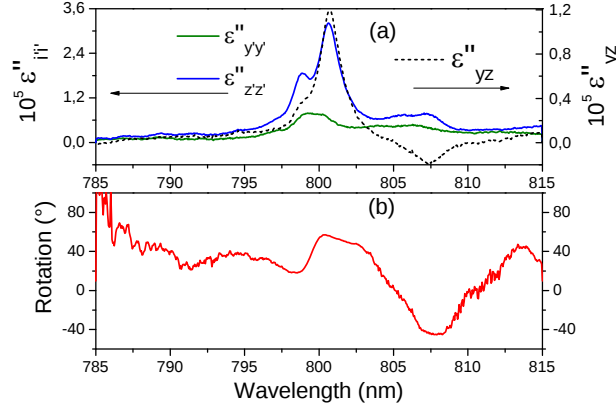


Figure 6. (a) $\mathcal{E}_{yz}''(\lambda)$ fourth absorption spectroscopic parameter (right scale) and $\mathcal{E}_{y'y'}''(\lambda)$ and $\mathcal{E}_{z'z'}''(\lambda)$ absorption spectroscopic parameters (left scale); (b) θ_0 -rotation of the $Y'Z'$ frame versus the absorption wavelength.

Figure 6(a) provides also (left scale) the $\mathcal{E}_{y'y'}''(\lambda)$ and $\mathcal{E}_{z'z'}''(\lambda)$ spectroscopic parameters related to the frame in which the permittivity tensor imaginary part is diagonal (equation (1)) and also involved in the approximated equation (6).

4.4. Optical emission

The experimental polarized photoluminescence was measured in the range from 1020 to 1090 nm at room temperature, by exciting the sample at 800 nm with a 200 mW InGaAs diode laser, which was modulated at 1 kHz. The luminescence was recorded in 90° geometry to minimize the influence of the laser pump and it was dispersed by a Jobin Yvon-Spex HR 460 monochromator, which has a focal length of 460 mm and a spectral resolution of 0.05 nm. The detector used was a cooled Hamamatsu NIR R5509-72 photomultiplier. The signals were processed by an EG&G 7265 DSP lock-in amplifier. For the lifetime measurements, the signals were treated with a computer-controlled Tektronik TDS-714 digital oscilloscope. The resulting spectra for Nd^{3+} transition $^4F_{3/2} \rightarrow$

$^4I_{11/2}$ are shown in figure 7(a) for N_p , N_m , N_g polarizations and figure 7(b) for a^* and c polarizations. The maximum emission peak is when $E \parallel N_p$, at 1052.4 nm, with a FWHM equal to 5 nm.

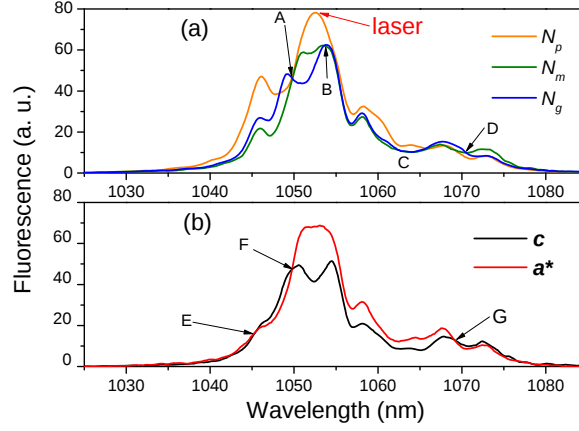


Figure 7. (a) Fluorescence intensity in N_p , N_m , N_g polarizations; (b) fluorescence intensity in a^* and c polarizations.

The Ladenberg-Fuchtbauer formula [42] is a consequence of the theory of Judd and Ofelt and it is limited by the approximation concerning to a population equality in the Stark sublevels, which do not apply to the case of neodymium. However, in this work, emission cross sections were calculated as in ref. [43], using the mentioned Fuchtbauer-Landenburg formula corrected by the luminescence branching ratios, β , reported by Gueugnon *et al.*, 1980 [44]. The maximum emission cross section for $E \parallel N_p$ at 1052.4 nm is equal to $3.26 \times 10^{-20} \text{ cm}^2$ and for $E \parallel N_m$ at 1056 nm is equal to $2.67 \times 10^{-20} \text{ cm}^2$. These values are relatively low in comparison with other NLO Nd matrixes such as, NYAB with $\sigma_{\text{emi}} = 20 \times 10^{-20} \text{ cm}^2$ [45] and Nd:YCOB with $\sigma_{\text{emi}} = 4.2 \times 10^{-20} \text{ cm}^2$ [46].

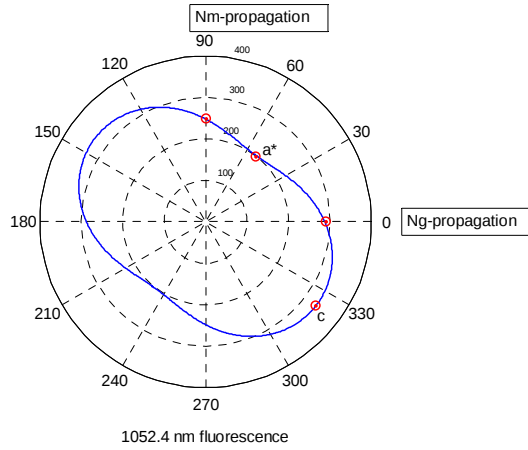


Figure 8. Full angular distribution of the 1052.4 nm fluorescence intensity for propagation in the N_m - N_g principal plane in extraordinary polarization.

The full angular distribution in the XZ principal plane of the extraordinary mode at this wavelength, calculated with equation (5), is shown in figure 8. It is obtained adjusting the three parameters: $I_y(1052.4 \text{ nm})$, $I_z(1052.4 \text{ nm})$ and $\mathcal{E}_{yz}''(1052.4 \text{ nm})$, the four experimental data being represented by the red circles. We can see that the emission extreme do not coincide with the propagation along the Y and Z principal axes.

The maximum emission of neodymium for this transition is at 1052.4 nm. The θ angle corresponds again to almost 35° and is almost coincident with the rotation angle for absorption at 800.6 nm, with light propagation along c and $E//a^*$. This is an interesting result for maximizing the gain in a crystal cut along this propagation direction, being optima the absorption and emission. This was not the case in Nd:YCOB crystals, where the rotation angles for absorption around 800 nm and emission around 1050 nm were not coincident [26].

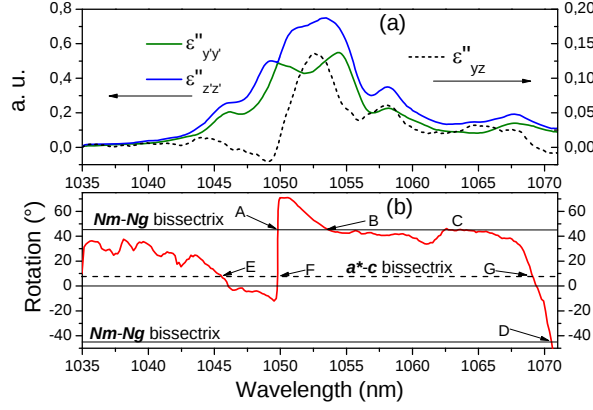


Figure 9. (a) $\epsilon''_{yz}(\lambda)$ fourth emission spectroscopic parameter (right scale) and $\epsilon''_{y'y'}(\lambda)$ and $\epsilon''_{z'z'}(\lambda)$ emission spectroscopic parameters (left scale); (b) θ_0 -rotation of the $Y'Z'$ frame versus the emission wavelength.

For each wavelength the obtained $\epsilon''_{yz}(\lambda)$ fourth spectroscopic parameter is provided in figure 9(a) (dashed line, right scale). The equivalent θ_0 -rotation of the $Y'Z'$ frame is visualized versus the emission wavelength in figure 9(b). The following guidance can improve the clarity of the latter figure. We have added the N_m-N_g bissectrix at $\pi/4$ rad = 45° rotation (and -45°) and the a^*-c bissectrix at 7.7° . These bissectrix cross the $\theta_0(\lambda)$ curve at two sets of points: A, B, C, D and E, F, G respectively. As it is explained in the section 4.1 last paragraph, these points are close to the corresponding points in figures 9(a) and 9(b) respectively where the extraordinary polarized spectra cross.

Figure 9(a) provides also (left scale) the $\epsilon''_{y'y'}(\lambda)$ and $\epsilon''_{z'z'}(\lambda)$ spectroscopic parameters related to the frame in which the permittivity tensor imaginary part is diagonal (equation (1)) and also involved in the approximated formula for emission (similar than equation (6)).

4.5. Laser emission

A KGdP:Nd crystal sample was pumped at 800.3 nm with a fibre coupled laser diode (from LIMO) perpendicularly to the natural (100) face, the N_p axis being horizontal. The faces are antireflection coated around 1060 nm. The absorbed pump power was 38%. The crystal was inserted in a plan-concave cavity constituted with a plane entrance mirror HR@1010/1080 nm and HT@800 nm and a concave output coupler with 2% transmission @1020/1080 nm and 50 mm radius curvature. The sample was hold and pressed between two pieces of copper. The thermal contact was improved by indium foils. The copper was cooled down near 11°C with a flux of water. A scheme of the set-up used in the laser experiments is shown in figure 10.

By moving horizontally and vertically the sample, a high optical quality area was found, leading to efficient lasing with 26% slope efficiency and Gaussian output beam (figure 11). The lasing wavelength was 1052.4 nm and the polarization was N_p axis (ordinary polarization). This is fully in agreement with the highest emission exhibited in the spectra of figure 7.

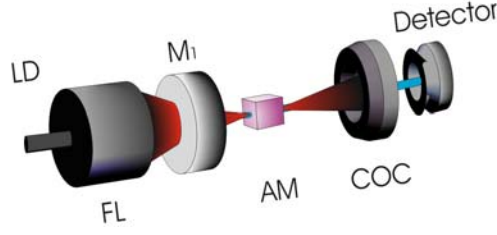


Figure 10. Set-up of the laser experiments (LD: laser diode, FL: Focusing lens, M₁: Plane mirror, AM: active material, COC: concave output coupler.).

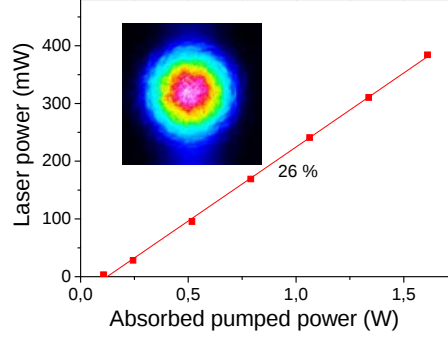


Figure 11. Laser output power at 1052.4 nm in N_p -polarization versus absorbed pump power. The inset shows the beam intensity distribution.

The slope efficiency obtained is lower than the obtained previously with Yb:KGdP (55 % slope efficiency) [25]. The enhancement of the lasing slope efficiency in Nd:KGdP could be obtained by optimizing the output coupler transmission in the lasing experiments and the propagation direction and the polarization of the pumping. Future work will be centered in this optimization and the obtaining of the suitable conditions for phase matching in order to demonstrate self-frequency doubling. Additional future work will be centered in the scintillation properties of Nd in this matrix by taking advantage of the low UV absorption edge of KGdP.

5. Conclusions

KGdP and Nd:KGdP single crystals, with Nd^{3+} contents of $0.288 \times 10^{20} \text{ at/cm}^3$ in the case of Nd doped crystals, have been grown. The transparency window of these crystals extends from 160 nm in the UV region to 4 μm in the IR region.

The Nd:KGdP crystal being monoclinic, its optical properties can be subjected to a rotation around the two-fold b-axis. We have determined that a slight rotation occurred for the dielectric frame in the 355-1064 nm range of wavelengths (a few tenths of degrees). We measured the absorption near 800 nm in the $^4I_{9/2} \rightarrow ^4F_{5/2}$ channel and the emission in the $^4F_{3/2} \rightarrow ^4I_{11/2}$ channel near 1050 nm. In addition to the three N_p , N_m , N_g usual polarizations, a fourth spectroscopic parameter was needed for a full description. This parameter corresponds to the wavelength dependence of the rotation around the **b**-axis of the frame which makes diagonal the imaginary part of the dielectric susceptibility. Lasing was obtained at 1052.4 nm in N_p polarization (ordinary wave) for propagation in the N_g - N_m principal plane.

The wide transparency window of this material together with its NLO properties makes it attractive for future studies on phase matching conditions for self-frequency doubling processes and the low UV cut-off is of interest for studying the scintillation properties of Nd in this matrix.

Acknowledgments

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