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Effect of dysprosium active ions on spectral properties of KGW single crystals

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ABSTRACT

Dysprosium (Dy) doped potassium gadolinium tungstate single crystals were grown by top seeded solution growth using K_2WO_4 as solvent. Two different concentrations of laser active ions were doped in the crystal. Crystals grown with lower growth rate using K_2WO_4 as solvent yielded better quality than that grown by $K_2W_2O_7$ as solvent. Growth conditions, like cooling rate and the rotation rate were optimized. Absorption studies confirm dominant absorption peaks in the visible as well as in near infrared regions. Photoluminescence reveals a strong yellow emission for the doped samples and the emission intensity of 3% Dy doped sample is 1.4 times higher than that of 1% Dy concentration in KGW. Raman spectra indicate the characteristic vibrational modes corresponding to the tungstate anion. The intensity of peaks in Raman spectra are increased with increase in concentration of Dy, in addition to a slight shift in Raman frequency.

1. Introduction

Visible lasers especially around the yellow region of the spectrum are gaining a lot of interest because of their potential applications in medical field including biomedicine and blood vessel disorders. Dysprosium (Dy) ions are good yellow source, because of a strong yellow luminescence due to $^4F_{9/2} \rightarrow {}^6H_{13/2}$ transitions. Recently, Dy^{3+} doped glass fibre was found to generate yellow lasers for such applications efficiently [1]. The yellow luminescence in Dy doped phosphors is also of interest for the generation of white light emission to be used for optical display systems [2,3]. In the case of solid state crystalline media, yellow lasers are achieved by the nonlinear conversion of infrared wavelength from rare earth ions like Nd and Yb. Still, there is a search for potential candidates as laser hosts to accommodate Dy^{3+} ions for potential yellow emission. Though, fluorides were considered in the early stages, but they have several growth difficulties compared to oxides. Oxides have been investigated recently to understand the spectroscopic properties of Dy^{3+} ions in the matrix [4–6].

Tungstates doped with rare earth ions have been investigated widely for variety of optical applications [7,8]. Double tungstate crystals with a general formula $ARe(WO_4)_2$ (A = Li, Na, or K, Re = rare-earth) are attractive laser host materials due to the excellent chemical durability in air atmosphere and the large rare-earth ion admittance [9–11]. In addition, these double rare earth tungstates display a number of fascinating peculiar properties that include optical and magnetic properties associated with a low symmetry of the crystal lattice [12]. Potassium based tungstates such as potassium gadolinium tungstate $KGd(WO_4)_2$ (KGW) single crystals have been used as a laser host for rare-earth ions, specially for Nd^{3+} ions because of its high efficiency $^4F_{3/2} \rightarrow {}^4I_{11/2}$ transition [13]. Rare earth activators enter the KGW lattice and substitutes Gd^{3+} ion because of the same valence and better matching of the ionic radius of Gd^{3+} ions with doped rare earth ions. Extensive research was focused on the tungstate crystals; because of its high cubic nonlinearity χ^3. It is possible to realize unconventional lasers, such as lasers with stimulated-Raman-scattering (SRS) or frequency self-conversion efficiently with these materials. Also, high thermal conductivity and high laser damage threshold make KGW more attractive for such nonlinear phenomena [14]. Dysprosium doped KGW single crystals were grown by top seeded solution growth method using $K_2W_2O_7$ as flux and the possibility of stimulated emission in the yellow wavelength region [15] was demonstrated with strong luminescence. Kaminskii et al. [16] have extensively studied the complex characterization of the crystallographic, optical and stimulated-emission properties of dysprosium doped $KGd(WO_4)_2$ and $KY(WO_4)_2$ crystals grown from $K_2W_2O_7$ flux and ascertained that the material can be used for lasing in the visible region. In the present work, growth of Dy doped KGW single crystals were carried out using K_2WO_4 as flux. The effect of this dif-

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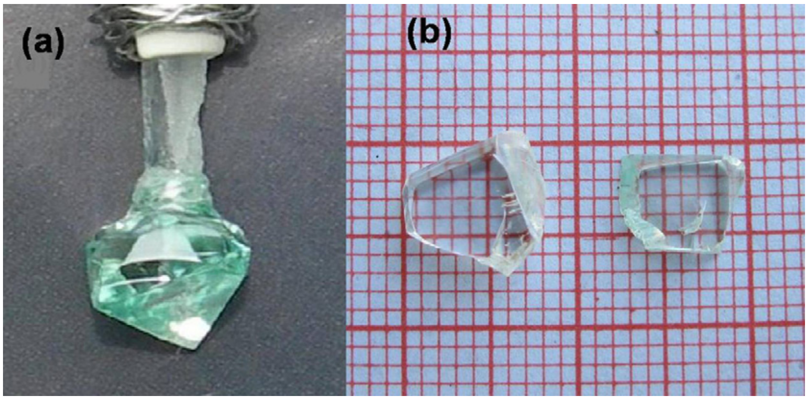

Fig. 1. (a) As grown Dy doped KGW single crystal. (b) Cut and polished 1 and 3% Dy:KGW single crystals.

ferent flux and the content of Dy-ions (1 and 3%) on the structural, optical and vibrational characteristics of KGW single crystals were analyzed.

2. Experimental details

Potassium based tungstate crystals have two polymorphic forms (i.e.) scheelite-type structure at high temperature and monoclinic structure in the room temperature. This structural-phase transition exists at a temperature below its melting point, so it is difficult to grow these crystals using the conventional Czochralski technique. As a consequence, they are grown using the high temperature solution growth method [17]. In the present work, KGW crystals were grown by top seeded solution growth method with K_2WO_4 as the flux. The starting materials were K_2CO_3, Gd_2O_3 and WO_3 (Alpha Aesar make) of high purity. They were taken in the ratio of 3:1:6, so that they can have K_2WO_4 as self flux as per the chemical reaction

$$3K_2CO_3 + Gd_2O_3 + 6WO_3 \rightarrow 2KGd(WO_4)_2 + 2K_2WO_4 + 3CO_2\uparrow$$

The chemicals were taken in a platinum crucible and were heat treated at 800 °C for 24 h for calcination process. Then the synthesized charge was taken and crushed again. The crushed chemicals were finally taken in a platinum crucible and were heated 50 °C above the expected saturation temperature in a resistive furnace. The temperature of the furnace was controlled by Eurotherm temperature controller having 0.1 °C resolution. Homogeneous melt was obtained by keeping the furnace at that temperature for 48 h. Dy_2O_3 was used as the source for Dy doped crystals. The concentration of Dy in the raw material was adjusted as 1 and 3 at.% in separate growth runs. Pure KGW seed was used for the growth of both pure and Dy doped KGW single crystals. After the melt was homogenized, the furnace was slowly cooled to attain super-saturation, by repeated seeding process. And, the super-saturation temperature was determined. The melt was slowly cooled at 0.1 °C/h and the seed was pulled at 1–2 mm/day. The pulling rate was maintained slightly lower during the growth of doped crystals to have a uniform distribution of the dopant ions. The rotation was maintained at 20 rpm. After the growth period was over, the furnace was cooled at 40 °C/h. This is to avoid any thermal shock that may lead to cracks in the crystal.

The grown crystals were cut and polished. The polished crystals were characterized with structural, optical and vibrational studies. The lattice parameters of pure and Dy doped KGW single crystals were determined using CAD-4 Enraf-Nonius single crystal X-ray diffractometer. Absorption studies were carried out between UV to near IR range using Cary 5E UV–vis–NIR spectrophotometer. Absorption coefficient values were calculated for various absorption peaks in the measured range of 200–2000 nm. He–Cd laser at 325 nm of 80 mW power was used as the pumping wavelength for photoluminescence measurements. The emission spectra for Dy doped KGW crystals were recorded in the visible region of 450–700 nm. The luminescence signals were collected perpendicular to the excitation beam to avoid spurious scattering of pump light. The vibrational characteristics of the crystals were analyzed by Raman spectrometer using Ar ion laser source of wavelength 488 nm. The scattered photons were collected through a double monochromator and a photomultiplier tube. All the spectroscopic measurements were carried out at room temperature.

3. Results and discussion

The growth procedure was optimized with K_2WO_4 as flux, for the growth of pure and Dy-doped KGW crystals. The pulling rate of the crystal (with K_2WO_4 as flux) was reduced to around 2 mm/day or lower compared to the pulling rate of 5 mm/day used with $K_2W_2O_7$ as flux [16]. Growth procedure with lower pulling rate improved the transparency of the crystals and also avoided flux inclusions and cracks. The slower pulling rate and the cooling rate were required for growing transparent and homogeneously doped crystals. The cut and polished crystals were optically transparent (Fig. 1). A piece of 2 mm × 2 mm small single crystal, cut from the boule was subjected to single crystal X-ray diffraction analysis. The single crystal XRD results show that both the pure and doped crystals belong to the monoclinic phase. The lattice parameters measured for the pure KGW single crystals are $a = 10.652$ Å, $b = 10.374$ Å and $c = 7.582$ Å, analogous with the results reported earlier by Pujol et al. [18]. In doped crystals, it is expected that Dy^{3+} ions may replace Gd^{3+} ion in the host matrix. Since the ionic radii of gadolinium and dysprosium are comparable, the strain produced by the dopant ion is negligible [19] and does not alter the crystalline structure or lattice parameters significantly. The unpolarized absorption spectra were measured in the range of 200–2000 nm. The absorption coefficient values of various peaks were calculated and the corresponding spectra are shown in Figs. 2 and 3 in two ranges. The peaks that are shallow for the 1% Dy doped KGW single crystals are quite significant when the concentration is increased to 3%. The absorption peaks were observed at 327, 352, 367, 388 and at 454 nm in the visible region of the spectrum; where as the near infra red region shows strong absorption at 754, 1094, 1295 and at 1689 nm. The absorption co-efficient values increase with

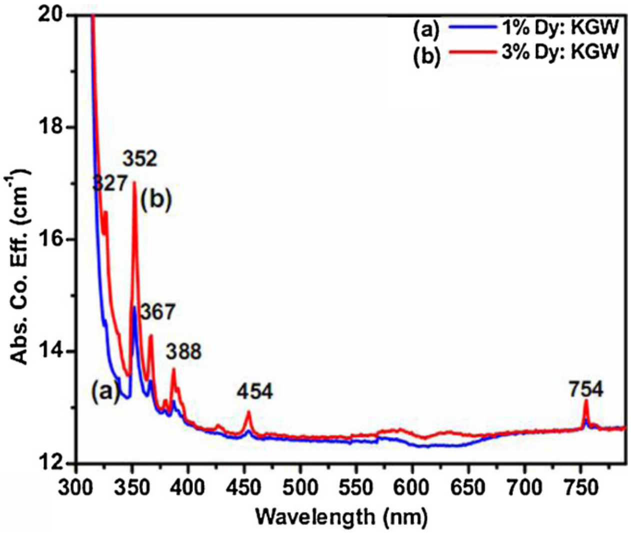

Fig. 2. Absorption spectra of 1 and 3% Dy doped KGW single crystals (from 300 to 800 nm).

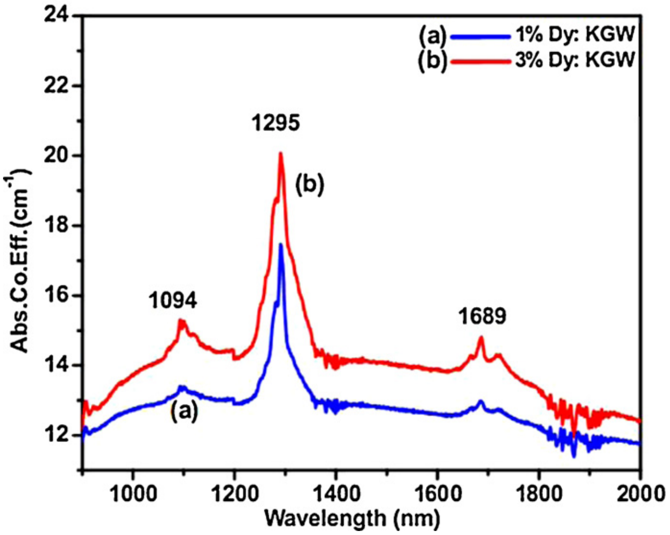

Fig. 3. Absorption spectra of 1 and 3% Dy doped KGW single crystals (from 900 to 2000 nm).

Table 1
Effective linewidth values at different emission bands for 1 and 3 at.% Dy doped KGW single crystals (λ_p is the peak wavelength).

λ_p (nm)	$\Delta\lambda_{\mathrm{eff}}$ (nm)	
	1 at.% Dy:KGW	3 at.% Dy:KGW
482	15.9	14.8
573	13.5	12.8
662	16.8	16.4

an increase in the concentration with a maximum absorption coefficient value of 20 cm^{-1} at 1295 nm for 3% Dy concentration. The absorption peak at 1295 nm corresponding to the transition from $^6H_{15/2}$ ground state to the excited level $^6H_{9/2}/^6F_{11/2}$ is very intense compared to other absorption peaks. The other absorption peaks correspond to the transitions from the $^6H_{15/2}$ ground level to the various excited levels of the Dy ion: 352 nm – $^4I_{11/2}/^6P_{7/2}$, 367 nm – $^4M_{19/2}$–$^4P_{5/2}$, 388 nm – $^4F_{7/2}$–$^4K_{17/2}$ and 454 nm – $^4I_{15/2}$, respectively. The absorption peaks at 754, 1094 and 1689 nm correspond to transitions to $^6F_{3/2}$, $^6H_{7/2}/^6F_{9/2}$, and to $^6H_{11/2}$ levels, respectively. A small peak at 427 nm has weak absorption, which corresponds to $^6H_{15/2}$–$^4G_{11/2}$ transition of Dy ion.

Photoluminescence (PL) spectra in the visible range were recorded using 325 nm He–Cd laser at room temperature. The samples showed strong yellow emission and the recorded PL spectra are shown in Fig. 4. The sharp intense peak is centered at 573 nm with two adjacent peaks at 482 nm and 662 nm. This 573 nm yellow emission is so strong that the Dy active ion can be used to generate yellow solid state laser. The observed luminescence peaks are due to the transitions from the excited energy level $^4F_{9/2}$ of the dysprosium ion. The transitions corresponding to the PL wavelengths are: 482 nm – $^4F_{9/2} \rightarrow {}^6H_{15/2}$, 573 nm – $^4F_{9/2} \rightarrow {}^6H_{13/2}$ and 662 nm – $^4F_{9/2} \rightarrow {}^6H_{11/2}$. The PL intensity increases with the concentration of Dy ions. The peak at 573 nm for 3% Dy:KGW is nearly 1.4 times intense than that of 1% Dy:KGW crystal. The effective line width of the emission bands can be calculated from the expression

$$\Delta\lambda_{\mathrm{eff}} = \frac{\int I(\lambda)d\lambda}{I_{\max}}$$

where the integral is over the emission band of each line and $I_{\max}$ is the peak emission intensity. The effective line width calculated for the intense band at 573 nm for 3% Dy concentration is 12.8 nm where as for 1% Dy:KGW sample, it is 13.5 nm. Similarly, the bands at 482 and at 662 nm also get slightly narrowed as the concentration is increased and the line width values are listed in Table 1. This narrow line width and high intensity enables high emission cross section for 3% Dy:KGW over the 1% Dy concentration. This proves the tight bonding of this material and enabling this crystal to be doped with high concentration of laser active ions. Another reason behind this decrease in the linewidth with increase in concentration is due to smaller ionic radius of Dy^{3+} ion (0.091 nm) which is replacing Gd^{3+} (0.1078 nm) ions [20,21].

The spontaneous Raman spectra recorded for Dy:KGW crystals using Ar ion laser are shown in Fig. 5. The potassium rare-earth double tungstates exhibit various types of vibrational modes in the complete range from 1000 cm^{-1} to 50 cm^{-1} [22]. These tungstates are formed by elongated chains of W_2O_8 along the C-axis in which W and O atoms, being the shortest pairs in the structure, form stable $WO_4{}^{2-}$ octahedral anionic complexes sharing the edges. The parallel chains are connected in the corners. They are formed as two WO_6 polyhedra and joined by double oxygen bridge. The Gd^{3+} ions in the host matrix form as a square antiprism, whereas the metal cation K$^+$ forms a distorted icosahedral coordination. In the doped crystals, Gd^{3+} ions are replaced by Dy^{3+} ions and this dopant incorporation has impact in the Raman vibrational frequency in

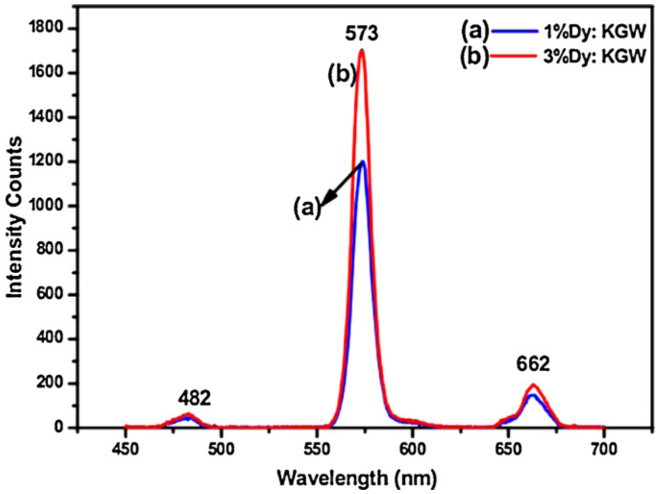

Fig. 4. Photoluminescence spectra of 1 and 3% Dy doped KGW single crystals.

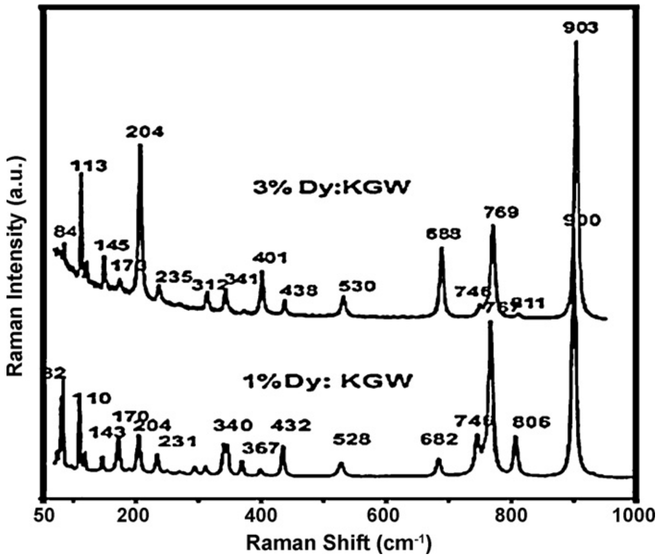

Fig. 5. Spontaneous Raman spectra of 1 and 3% Dy doped KGW single crystals.

the range of 100–260 cm^{-1} [22]. Raman spectra as recorded for 1 and 3% Dy:KGW single crystals show that the peaks are slightly shifted on the higher energy side of the spectrum as the concentration is increased. The intense Raman peaks observed in the range of 500–935 cm^{-1} are due to the various stretching vibrations of the tungstate polyhedra. The more intense peak centered at 903 cm^{-1} with a narrow line width of around 6 cm^{-1} is due to the strong stretching vibrations of the W=O bond. This high Raman scattering efficiency with the narrow linewidth makes this material an efficient material for the generation of cascade Raman emissions by stimulated Raman scattering phenomenon. Another stretching mode vibration involving W–O antiphase motion generates another intense Raman peak at 769 cm^{-1} with the linewidth of 7 cm^{-1}. The sharp narrow lines at 903 and 769 cm^{-1} with the respective linewidths of 7 and 6 cm^{-1} match well with that of the pure bulk KGW single crystals. The results confirm that the dopant ions do not have any effect on the intense vibrational modes and thus makes this material an efficient Raman converter with a very high Raman gain coefficient [23]. The peak at 530 cm^{-1} represents the O–W–O stretching vibrations. The peak at 438 and 401 cm^{-1} represents the out of plane bending modes whereas the peaks centered at 341 and at 312 cm^{-1} are ascribed to the in plane O–W–O bending vibration mode. The peaks in the lower frequency range are attributed to the translational lattice vibrations involving the rare earth ion including Gd^{3+} and Dy^{3+}. The intensity of the peaks in the lower range increases with the concentration but there is no significant change in the peak position. The combined emission and vibrational results confirm that KGW can be doped with high concentration of Dy^{3+} ions towards the generation of yellow lasers with additional lasing channels by SRS phenomenon.

4. Conclusions

Dysprosium doped $KGd(WO_4)_2$ single crystals were grown with top seeded solution growth method with K_2WO_4 as flux. The optimized growth parameters yielded transparent single crystals. The influence of dopant ion concentration on structural, optical and vibrational characteristics of the crystals was analyzed. The structural studies confirm that there is no change either in the crystal structure or in lattice parameters because of Dy activator ions. The absorption studies reveal many absorption peaks, which were correlated to dopants and correspond to various energy levels of trivalent dysprosium ion. The strong yellow emission with a narrow linewidth for the doped samples of different concentration can be utilized for fabricating compact diode pumped solid state visible lasers. The vibrational analysis indicates different vibrational modes in the crystal structure and an insignificant shift in the Raman peaks for different concentration of dopants. The intense and narrow Raman lines for the Dy:KGW make it an interesting material for an efficient stimulated Raman scattering material in the yellow region.

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