Vibrational properties of Nd\(^{3+}\), Eu\(^{3+}\), Er\(^{3+}\) and Ho\(^{3+}\) doped KGd(WO\(_4\))\(_2\) single crystals studied by Raman scattering method

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Abstract

The polarized Raman spectra of KGd(WO\(_4\))\(_2\) single crystals doped with rare earth ions Nd\(^{3+}\), Eu\(^{3+}\), Ho\(^{3+}\) and Er\(^{3+}\) were carried out in the range of internal and external vibrations 20 – 1000 cm\(^{-1}\) at room temperature. No significant influence of rare earth ions doping on the band positions was observed. However, most of detected in \(y(xx)z\) and \(y(xy)z\) scattering geometry Raman bands exhibit depolarization. The highest depolarization ratio is observed for the bands at 526, 684 and 766 cm\(^{-1}\) assigned to the stretching vibrations of the WO\(_6\) oxygen bridge bonds. While, the bands at 348, 371 and 899 cm\(^{-1}\) assigned to the bending and stretching vibrations of WO\(_4\)\(^2-\) tetrahedra, are almost fully polarized for all investigated crystals. The depolarization of bands is due to distortion of WO\(_4\)\(^2-\) tetrahedra and WO\(_6\) bridge bonds forming the structure of KGd(WO\(_4\))\(_2\). Moreover, the lowest degree of depolarization for analyzed bands was observed for KGd(WO\(_4\))\(_2\) : Nd crystals, which exhibits less affected vibrational spectra by doping ions than other investigated crystals.

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1. Introduction

Potassium gadolinium tungstate crystals KGd(WO\(_4\))\(_2\) (KGW) doped with rare earth ions are very attractive solid state laser materials [1]. The optical and spectroscopic properties
of tungstates have been already investigated [2–15]. However, it is still a little known on the influence of the doping ions such as \( \text{Nd}^{3+}, \text{Eu}^{3+}, \text{Er}^{3+} \), or \( \text{Ho}^{3+} \) on their vibrational properties.

KGW crystals belong to the monoclinic structure with \( C2/c = C_{2h}^6 \) space group \((Z = 4)\) at room temperature. The lattice cell parameters were found to be: \( a = 10.652 \text{ Å}, b = 10.374 \text{ Å}, c = 7.582 \text{ Å}, \beta = 130.80^\circ \) [16]. In KGW structure the tungsten and oxygen atoms form octahedral anionic complexes with \( C_1 \) symmetry. The potassium \( \text{K}^+ \) and gadolinium \( \text{Gd}^{3+} \) ions, occupy the equivalent crystallographic positions having \( C_2 \) symmetry with random distribution. This can lead to the short range ordering in the anionic layers. The structure of KGW is formed by chains of \( W_2O_8^{4+} \) ions along the \( c \)-axis and connected in their corners by oxygen atoms with two \( \text{W}–\text{O} \) distances equal to 1.758 Å and 2.359 Å (WOW oxygen bridge bonds). The dimers \( W_2O_8^{4+} \) are formed by two \( \text{WO}_4^{2−} \) ions, which are connected by four \( \text{W}–\text{O} \) bonds with two different lengths equal to 1.955 Å and 2.109 Å (WOOW double oxygen bridge bonds). In the wolframite structure these four \( \text{W}–\text{O} \) bonds have the same length and the two equivalent oxygen bridges in the unit cell possess a centre of inversion. In the case of KGW crystals a significant distortion of WOOW bridge bonds occurs and the inversion center is not preserved. Moreover, the two different crystallographic nonequivalent orientation of the WOOW oxygen bridge bonds exist in KGW crystal structure [15]. The lengths of the remaining two \( \text{W}–\text{O} \) bonds are equal to 1.747 Å and 1.825 Å [2]. Along the \( b \) axis the tungstate – oxygen layers are alternate with the cationic layers created by \( \text{K}^+ \) and \( \text{Gd}^{3+} \) ions. In the rare earth ions doped KGW crystals the \( \text{Gd}^{3+} \) ions can be efficiently substituted by \( \text{Nd}^{3+}, \text{Eu}^{3+}, \text{Er}^{3+} \), or \( \text{Ho}^{3+} \) ions [2,10]. For the doping concentration used in this work the crystal structure does not change. The slight change in the cell parameters observed can be the consequence of the different ionic radii of \( \text{Nd}^{3+}, \text{Eu}^{3+}, \text{Gd}^{3+}, \text{Er}^{3+} \), or \( \text{Ho}^{3+} \) ions equal to 1.15, 1.13, 1.11, 1.05 and 1.04 Å, respectively [17].
In this work we present the study of the vibrational properties of the Nd\(^{3+}\), Eu\(^{3+}\), Er\(^{3+}\) or Ho\(^{3+}\) doped KGW crystals by Raman scattering method. Similarities in Raman polarized spectra of investigated crystals was observed. However, the structure and spectral parameters of selected bands allow us to determine the influence of doping ions on stretching and bending vibrations of WO\(_2^2\) tetrahedra and WOOW oxygen bridge bonds on KGW crystal structure.

2. Experimental

KGW : Nd, KGW : Eu, KGW : Er and KGW : Ho single crystals were obtained using the Top Seeded Solution Growth method from 25 mol % solutions of KGW in K\(_2\)W\(_2\)O\(_7\) on [010] oriented seeds. The detailed description of the used technique can be found elsewhere [16]. The doping concentration of Nd\(^{3+}\), Eu\(^{3+}\), Ho\(^{3+}\) or Er\(^{3+}\) ions was 3 at.%, 5 at.%, 3 at.% and 1 at.%, respectively. The crystallographic orientation of the samples was performed by the Laue method and analytical use of the stereographic Wulff net, described in details by Michalski et al. [18]. The oriented samples of sizes 5 mm × 4 mm × 3 mm with faces perpendicular to the [100], [010] and [001] directions were used to collect the polarized Raman spectra. The scattered light was analyzed using double-grating monochromator with the spectral slit – width 2 cm\(^{-1}\). The spectra were excited with \(\lambda = 488\) nm line of ion argon laser at 90° scattering geometry in the spectral range 20 – 1000 cm\(^{-1}\). The fitting procedure, considering Bose–Einstein population factor was applied to obtain the band parameters of Raman spectra.

3. Results and discussion
The crystal structure of KGW : Nd, KGW : Eu, KGW : Ho and KGW : Er, are isomorphous with KGW structure. The primitive unit cell of KGW crystals includes two Kgd(WO₄)₂ units and contains 24 atoms giving 72 fundamental vibrations. From the factor group analysis of the zone-center modes for monoclinic structure (C2/c = C2h) the activity of the 3 acoustic modes Aₐ + 2Bₐ, 15 translational modes 2Aₐ + 4Bₐ + 4Aₐ + 5Bₐ, 6 librational modes 3Aₐ + 3Bₐ, and 48 internal modes 12Aₐ + 12Bₐ + 12Aₐ + 12Bₐ is predicted. Among them 17Aₐ + 19Bₐ are Raman-active modes [19]. The detailed assignment of the modes for Kgd(WO₄)₂ crystals was proposed by Macalik et al. [15].

For tungstate crystals, in which WO₄²⁻ ions form isolated tetrahedra, the internal stretching vibrations occur in the 750 – 1000 cm⁻¹ range, while the internal bending vibrations occur in the 250 – 430 cm⁻¹ range. Therefore, Raman spectra of KGW crystals are more complicated due to some bands activated by the WOOW and WOW oxygen bridge bonds vibrations in these spectral ranges.

To determine the influence of the doping ions Nd³⁺, Eu³⁺, Er³⁺ or Ho³⁺ of the KGW crystals on Raman spectra, the crystals have been investigated under the same experimental conditions at room temperature. To detect Aₐ and Bₐ modes of rare earth doped KGW crystals the Raman spectra were collected in χ(xx)z and χ(xy)z scattering geometries, respectively. The polarized Raman spectra of rare earth doped KGW crystals obtained in the 20 – 1000 cm⁻¹ spectral range at room temperature are presented in Fig. 1.

Fig. 1

As it can be seen from Fig.1 the Raman spectra of KGW : Eu, KGW, KGW : Ho and KGW : Er crystals are almost identical suggesting that these compounds are isostructural in relation to X-ray investigations [2, 12]. However, the spectra of KGW : Nd differ from the rest, mainly in the relative intensity of the detected bands. It was found that the experimentally determined depolarization of selected bands is stronger for bands related to
oxygen bridge bonds WOOW than for \( \text{WO}_4^{2-} \) tetrahedral vibrations. The position of the majority of the modes are slightly different for Nd\(^{3+} \), Eu\(^{3+} \), Ho\(^{3+} \) or Er\(^{3+} \) doped KGW crystals. However, the coupling between the vibrations of different molecular groups in the modified by doping ions Nd\(^{3+} \), Eu\(^{3+} \), Ho\(^{3+} \) or Er\(^{3+} \) ions KGW crystal lattice leads to the change in the structure some of vibrational modes, particularly in their relative intensity values.

The detected Raman spectra of rare earth doped KGW crystals cover the range of external and internal vibrational motions. The detailed analysis of the Raman spectra allows us to assign the Raman bands as \( A_g \) or \( B_g \) modes. However, as it can be also seen from Fig. 1 most of them are not fully polarized, being active both in \( y(xz)z \) and \( y(xy)z \) spectra. The \( \text{WO}_4^{2-} \) tetrahedra vibrational modes appear in Raman spectra in the range 270 – 1000 cm\(^{-1} \). As it can be also seen from Fig. 1 the very intense, sharp peak attributed to symmetric stretching vibrations of the \( \text{WO}_4^{2-} \) tetrahedra appears at about 899 cm\(^{-1} \) as \( A_g \) mode. The stretching vibrations of \( \text{WO}_4^{2-} \) group appear in the spectral range 740 – 810 cm\(^{-1} \). The polarized \( A_g \) band positioned at 743 cm\(^{-1} \) is attributed to coupling stretching vibration of \( \text{WO}_4^{2-} \) and WOOW, while the \( A_g \) band at 766 cm\(^{-1} \) to the stretching vibration of WOOW oxygen bridge. The \( B_g \) modes detected at 754 and 805 cm\(^{-1} \) are attributed to stretching vibrations of WOOW and WOW bridge bonds, respectively. In the spectral range 400 – 700 cm\(^{-1} \) the stretching and bending vibrations of WOOW and WOW were observed. Depolarized \( B_g \) and \( A_g \) bands at 526 and 684 cm\(^{-1} \), respectively are assigned to the stretching vibrations of the WOOW oxygen bridge bonds. Moreover, the \( A_g \) modes positioned at about 684 cm\(^{-1} \) for KGW : Nd, KGW and KGW : Ho crystals change into \( B_g \) symmetry for KGW : Eu and KGW : Er crystals. The deformation bending vibrations of \( \text{WO}_4^{2-} \) tetrahedra appear in the spectral range 270 – 380 cm\(^{-1} \). The bending vibrations of \( \text{WO}_4^{2-} \) are recorded at 348 and 372 cm\(^{-1} \) as \( B_g \) modes, and the mode observed at 342 cm\(^{-1} \) is recorded as \( A_g \) mode. The bands positioned at 314 and 401 cm\(^{-1} \)
are attributed to the out-of-plane and in-plane bending of WOW, respectively. Moreover, the bands connected with bending vibrations of the oxygen WOOW bridge bonds appear at 272, 278 and 298 cm$^{-1}$. Below 260 cm$^{-1}$ the lattice modes (librations of WO$^{2-}_4$ ions and translations of WO$^{2-}_4$, K$^+$, Gd$^{3+}$ and W$^{6+}$ ions), in-plane and out-of-plane bending of WOOW and WOW bridge bonds, wagging vibrations of the whole W$_4$O$_{20}$ complex have been observed in Raman spectra. The dominant band in this spectral range is attributed to the strong translational mode of WO$^{2-}_4$ ions located at 89 cm$^{-1}$. Most of the bands in this spectral range are active with higher intensity in $\gamma(xz)z$ geometry, except for the modes at 80, 103, 191 and 252 cm$^{-1}$, which are fully polarized and recorded in $\gamma(xy)z$ geometry. The band positions given above are determined for KGW crystals. The positions of most of the described modes are slightly different for KGW : Nd, KGW : Eu, KGW : Ho and KGW : Er crystals.

In case of KGW : Nd the intensity ratio of the bands at 754 and 766 cm$^{-1}$, detected in $\gamma(xy)z$ geometry, is reverse than in other crystals. This results from the higher contribution of stretching vibrations of WO$^{2-}_4$ tetrahedra than WOOW group to intensity of 754 cm$^{-1}$ mode, in opposite manner than in other crystals. Moreover, the intensity ratio of the bands at 350 and 370 cm$^{-1}$, related to the bending vibrations of WO$^{2-}_4$ tetrahedra, is also reverse than in other crystals. While, the bending vibrations of WO$^{2-}_4$ tetrahedra positioned at 342 cm$^{-1}$ have the highest intensity for KGW : Nd crystals. The different structure of these modes, in the case of KGW : Nd crystals, expresses the change in the activity of vibrations of WO$^{2-}_4$ tetrahedra in the region of the bending vibration. The bands at 526 and 684 cm$^{-1}$ are stronger polarized in comparison to other crystals, showing evidently the $B_g$ and $A_g$ symmetry, respectively. The intensive, strongly depolarized $A_g$ mode at 206 cm$^{-1}$ related to translational vibration of Gd$^{3+}$ ions appears in KGW : Nd with relatively higher intensity. The Nd$^{3+}$ ions occupy in KGW crystals the same position as Gd$^{3+}$ ions. Because of the relatively high difference in ionic
radius between $\text{Gd}^{3+}$ and $\text{Nd}^{3+}$ ions, which can lead to the change in the local charge distribution, the essential increase of this band intensity occurs. While, the bands at 235 cm$^{-1}$ related to translational vibrations of $\text{K}^+$ ions do not present differences in the spectral parameters in any investigated crystals. We can conclude that the occupation of $\text{K}^+$ ionic sites are not disturbed by the doping of $\text{Nd}^{3+}$, $\text{Eu}^{3+}$, $\text{Ho}^{3+}$ or $\text{Er}^{3+}$ ions in KGW structure.

The spectral analysis of the bands shows minor frequency changes but most of them show significant intensity changes. To describe these phenomena we determined the depolarization $\rho$ as the intensity ratio $I_{xy}/I_{xx}$ and $I_{xx}/I_{xy}$ of Raman bands detected in $y(xx)z$ and $y(xy)z$ scattering geometry for $A_g$ and $B_g$ modes, respectively [13]. The zero value of $\rho$ means the fully polarized $A_g$ or $B_g$ modes, while for the used scattering geometries the maximum values is equal $\rho = 6/7$. The depolarization $\rho$ for selected Raman bands of KGW : $\text{Nd}$, KGW : $\text{Eu}$, KGW, KGW : $\text{Ho}$ and KGW : $\text{Er}$ crystals are presented in Fig. 2.

As it is seen from Fig. 2 the degree of the depolarization of selected modes slightly changes in the order $\text{Er}^{3+} < \text{Ho}^{3+} < \text{Gd}^{3+} < \text{Eu}^{3+}$ ionic radius increase, while for KGW : $\text{Nd}$ depolarization changes in different manner. The 348 and 371 cm$^{-1}$ bands assigned to bending vibrations of $\text{WO}_4^{2-}$ are almost fully polarized as $B_g$ modes with low depolarization $\rho$ equal to 0.09 – 0.31 and 0.08 – 0.34, respectively (slightly increases in the order $\text{Er}^{3+} < \text{Ho}^{3+} < \text{Gd}^{3+} < \text{Eu}^{3+} < \text{Nd}^{3+}$ ionic radius increase). The depolarization of the $A_g$ mode at about 899 cm$^{-1}$, assigned to the highly symmetric stretching vibrations of the $\text{WO}_4^{2-}$ tetrahedra, is almost the same for all investigated crystals with the value $\rho$ in the range from 0.27 to 0.39. The $A_g$ band positioned at 744 cm$^{-1}$, attributed to coupling stretching vibration of $\text{WO}_4^{2-}$ and WOOW oxygen bridge bonds, have highest depolarization $\rho$ equal to 0.45 for KGW : $\text{Nd}$ crystals, while 0.18 – 0.29 for other crystals. The strongly depolarized bands at 529 cm$^{-1}$ being active as $B_g$ mode with
depolarization $\rho$ equal to 0.51 – 0.64 and the band at 685 cm$^{-1}$ as $B_g$ for KGW and KGW : Ho and $A_g$ mode for KGW : Nd, KGW : Eu and KGW : Er crystals with depolarization $\rho$ equal to 0.48 – 0.63, are assigned to the in-plane stretching vibrations of the WOOW oxygen bridge bonds. The $A_g$ band at 766 cm$^{-1}$ assigned to the stretching vibration of WOOW oxygen bridge are also strongly depolarized with high degree of depolarization $\rho$ equal to 0.41 – 0.60. The depolarization of the selected bands for KGW : Nd is in the small range from 0.27 (for 899 cm$^{-1}$ band) to 0.34 (for 371 cm$^{-1}$), which indicates the higher symmetry of $WO_4^{2-}$ tetrahedra (close to $T_d$ symmetry of free $WO_4^{2-}$ ion) in this crystal than for others. While, the depolarization of the bands related to WOW and WOOW oxygen bridge bonds are almost the same as for other crystals. The lower depolarization of bands positioned at 348, 371 and 899 cm$^{-1}$ related to bending and stretching vibrations of $WO_4^{2-}$ tetrahedra is caused by to the slight distortion of $WO_4^{2-}$ tetrahedra at room temperature. This can lead to the lowering of symmetry of $WO_4^{2-}$ ions and in consequence depolarization of related bands. It was also found for other tungstates that the Ln$^{3+}$ cations surrounding the $WO_4^{2-}$ anions affect the internal vibrations of these anions [20].

4. Conclusions

The polarized Raman spectra of KGW single crystals doped with rare earth ions Nd$^{3+}$, Eu$^{3+}$, Ho$^{3+}$ or Er$^{3+}$ were investigated. No significant influence of rare earth ions doping on the band positions was observed. However, most of detected in $y(xx)z$ and $y(xy)z$ scattering geometry Raman bands exhibit depolarization due to distortion of $WO_4^{2-}$ tetrahedra and WOOW bridge bonds forming the structure of pure and doped KGW crystals. The highest degree of depolarization is observed for the bands at 526, 684 and 766 cm$^{-1}$ assigned to the
stretching vibrations of the WOOW oxygen bridge bonds for all investigated crystals, which results from the existence of two different crystallographic nonequivalent orientation of the WOOW oxygen bridge bonds and local distortion of these molecular groups in the crystal structure. Whereas, the bands at 348, 371 and 899 cm⁻¹, assigned to bending and stretching vibrations of WO₄²⁻ tetrahedra, have very low degree of depolarization for all investigated crystals. We conclude that the distortion of WOOW oxygen bridges is evidently stronger than distortion of relatively more rigid WO₄²⁻ tetrahedra for all investigated crystals. Moreover, the lowest degree of depolarization for analyzed bands was observed for KGW : Nd crystals.

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References


**Figure Captions**

Fig. 1. Raman spectra of KGW : Nd, KGW : Eu, KGW, KGW : Ho, KGW : Er crystals for $y(xx)z$ (a) and $y(xy)z$ (b) scattering geometry.

Fig. 2. Depolarization of 899, 766, 745, 684, 526, 371 and 348 cm$^{-1}$ bands of KGW : Nd, KGW : Eu, KGW, KGW : Ho, KGW : Er crystals.
Depolarization

Rare earth ionic radius ($\text{A}^\circ$)

899 cm$^{-1}$ Ag
766 cm$^{-1}$ Ag
743 cm$^{-1}$ Ag
684 cm$^{-1}$ Ag
526 cm$^{-1}$ Bg
371 cm$^{-1}$ Bg
348 cm$^{-1}$ Bg