# Phonon, optical and dielectric properties of RbNd(WO$_4$)$_2$ laser crystal

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## ARTICLE INFO

## ABSTRACT

Polarized Raman, IR, optical and dielectric studies of RbNd(WO$_4$)$_2$ single crystal have been performed. Symmetries of the observed Raman and IR modes have been established and their assignment to respective motions of atoms has been proposed. We have shown that the phonon properties of RbNd(WO$_4$)$_2$ are very similar to the phonon properties of KGd(WO$_4$)$_2$ but significantly different from properties of isostructural KLu(WO$_4$)$_2$ and KYb(WO$_4$)$_2$. The intensity parameters determined for RbNd(WO$_4$)$_2$ by means of the Judd–Ofelt theory are the most similar to those reported for KLu(WO$_4$)$_2$:Nd$^{3+}$. Dielectric measurements have revealed that this crystal exhibits low DC conductivity with the activation energy 1.02 eV up to 773 K and 1.22 eV at higher temperatures.

## 1. Introduction

Double tungstates of general formula M$^I$M$^{III}$(WO$_4$)$_2$ (M$^I$ = Na, K, Rb; M$^{III}$ = rare earth ion) constitute large family of compounds, which have found application as efficient laser materials [1–4]. They are also characterized by large third-order nonlinear optical susceptibility, which makes them useful for application as efficient Raman converters [5–7].

RbNd(WO$_4$)$_2$ crystallizes in the monoclinic structure, space group C2/c, which is isostructural with α-KY(WO$_4$)$_2$ [8]. Raman studies were reported for KM$^{III}$(WO$_4$)$_2$ crystals (M$^{III}$ = Sm-Lu, Y) [2,3,9–12]. However, the presented spectra were not very well polarized, which made it difficult to locate weak B$_g$ modes. IR spectra were presented mainly for polycrystalline samples [3,10,12,13]. Polarized IR spectra were analysed previously by us for KGd(WO$_4$)$_2$, KY(WO$_4$)$_2$, KSm(WO$_4$)$_2$ and KLu(WO$_4$)$_2$ but due to small size of the studied crystals, the polarization behaviour could not be well observed, especially in the low wavenumber region [9,10,12]. To the author's knowledge, Raman studies have not been yet reported for any rubidium rare-earth tungstate, probably due to difficulties in growing large single crystals of these materials. There are also no reports on polarized IR studies for the rubidium crystals and IR spectra of the polycrystalline sample were published only for RbGd(WO$_4$)$_2$ [13].

In the present paper, we report polarized Raman and IR studies of RbNd(WO$_4$)$_2$ single crystal grown by Top Seeded Solution Growth (TSSG) technique. The knowledge of phonon wavenumbers is important for correct interpretation of emission and absorption spectra as well as evaluation of the crystal for possible application as a Raman converter. The large size of the crystal allowed as obtaining high quality data both for Raman and IR-active modes. The obtained results have been compared with the literature data reported for the potassium rare-earth tungstates in order to propose the assignment of modes. We also report results of Judd–Ofelt analysis for this material as well as studies of dielectric properties.

## 2. Experimental

According to Postupaeva et al. rubidium neodymium tungstate melts congruently at 1055 °C [14]. It allows growth of this material by means of standard Czochralski technique. Unfortunately, due to two phase transitions at 1020 and 840 °C, single crystals of the low temperature α-RbNd(WO$_4$)$_2$ phase having monoclinic structure cannot be obtained in this way. Such a behaviour is typical for double potassium rare-earth tungstates KRE(WO$_4$)$_2$ (RE = Y, Gd, Lu, Yb, Ho). All the materials melt congruently above 1050 °C, but near 1000 °C they show irreversible phase transition. The high temperature phases can be grown from stoichiometric melt, but they do not transform into the low-temperature monoclinic phase, which is commonly used in laser applications. To overcome this obstacle Top Seeded Solution Growth from K$_2$W$_2$O$_7$ solvent is used to obtain single crystals of the desired crystals. Due to good solubility of double tungstates in K$_2$W$_2$O$_7$ up to 40 mol% and broad temperature range of the crystallization it is relatively easy to grow single

crystals having volume of tens of $cm^3$. In case of $RbNd(WO_4)_2$ the crystallization area of $\alpha$-phase is much smaller. First of all, according to phase diagram of $RbNd(WO_4)_2$–$Rb_2W_2O_7$ system the area of crystallization is limited from 9.5 mol% ($\alpha \rightarrow \beta$ transformation at 840 °C) to 4.5 mol% ($RbNd(WO_4)_2$–$Rb_2W_2O_7$ eutectic formation at 640 °C) [14]. Moreover, the solubility curve of $RbNd(WO_4)_2$ in $Rb_2W_2O_7$ is strongly nonlinear, the most of the material precipitates from the solution near the temperature of the $\alpha \rightarrow \beta$ phase transition. This makes it necessary to crystallize $\alpha$-$RbNd(WO_4)_2$ close to this temperature and is a potential threat of destroying the seed due to the $\alpha \rightarrow \beta$ phase transition. As a result very precise temperature conditions control should be used.

The crystallization of $\alpha$-$RbNd(WO_4)_2$ was carried out in a two-zone resistance furnace. The crystallization set was similar to that used in crystallization of $KHo(WO_4)_2$ and its detailed description can be found elsewhere [15]. The crystals were grown on seeds obtained by spontaneous crystallization under conditions of low-temperature gradient (~2 °C/cm). The rotation rate was equal to 20 rpm, no pulling was used, the temperature of the melt was lowered at a rate of 0.05 °C/h. Owing to mild temperature conditions the crystals grew in the volume of the melt and were confined with crystallographic faces. At the end of the crystallization the as-grown crystals were pulled up from the melt and cooled down at a rate of 5 °C/h.

The samples for the Raman and IR studies were prepared by cutting the crystal along the crystallographic axis *b* and *c*, and the direction perpendicular to these axes. Then the samples were polished and had good optical quality. They were transparent with a violet colour.

Polycrystalline infrared spectra were measured with a Biorad 575C FT-IR spectrometer as KBr pellets in the $1500–400\ cm^{-1}$ region and in Nujol suspension for the $500–40\ cm^{-1}$ region. Polarized IR spectra were measured in the $E\|x$, $E\|y$ and $E\|z$ geometries with the same spectrometer using fixed angle specular reflectance accessory. The *x*, *y* and *z* axes correspond to the three orthogonal principal crystallooptic axes $N_m$, $N_p$ and $N_g$, respectively. For this monoclinic crystal $N_p$ is parallel to the $C_2$ symmetry axis, which coincides with the crystallographic *b* axis. The orientation of the $N_g$ and $N_m$ axes was determined using a polarizing microscope. $N_g$ is located at 28° with respect to the *c* crystallographic axis where the angle of rotation is measured in the clockwise direction when the positive end of the *b* axis is pointing towards the observer, and the $N_m$ is perpendicular to $N_g$ and $N_p$.

The Raman spectra were obtained with a triple-grating spectrometer Jobin Yvon T64000, equipped with a $N_2$-cooled charge coupled device (CCD) detection system. The line 514.5 nm of an argon laser was used as excitation. An Olympus microscope lens with a focal distance f-20.5 mm and a numeric aperture of N.A = 0.35 was used to focus the laser beam on the sample surface.

The optical absorption spectra were measured at room temperature in the range of 33,000–3300 $cm^{-1}$ (300–3000 nm) using a Cary Varian 5E UV–Vis–NIR spectrophotometer. Polarized spectra were recorded with Glan–Thomson polarizers inserted in the sample and reference beams of the spectrophotometer. The spectral resolution was 0.1 nm in the visible and 0.8 nm in the near infrared region. The crystal with thickness of 1.6 mm was measured to obtain information on the transitions with weak intensities. Then the crystal was cut and polished to 0.28 mm thickness and this sample was used in further measurements.

Dielectric properties of $RbNd(WO_4)_2$ crystals were measured at frequency range from $10^{-1}$ to $10^6$ Hz using an Alpha analyser from Novocontrol GmbH equipped with NorECs SA high temperature sample heating system. The measurements were performed at dry air atmosphere with solid platinum electrodes at constant temperatures with a step of 20 K in the 370–1070 K range.

## 3. Results

### 3.1. Raman and IR

$RbNd(WO_4)_2$ structure consists of three kinds of polyhedra. These are octahedron, dodecahedron and icosahedron around W, Nd and Rb, respectively [8]. The neodymium and alkali metal ions lie on twofold axes and the tungsten atoms are in general position [8]. Two $WO_6$ octahedra are joined by sharing edges forming $W_2O_{10}$ unit connected by double oxygen bridge with the W–O bonds of 1.961 and 2.097 Å [8]. These units form a double chain along the crystallographic *c* axis by sharing vertex oxygen. In this way, a single oxygen bridge is formed between the $W_2O_{10}$ units with shorter and longer W–O distance of 1.782 and 2.347 Å, respectively [8].

The primitive cell of the C2/c structure of $RbNd(WO_4)_2$ comprises two formula units and the total Brillouin zone center modes include $17A_g + 19B_g + 17A_u + 19B_u$. The $A_g$ and $B_g$ modes are Raman active, and $A_u$ and $B_u$ modes are IR active. Translational motions of Rb, Nd and W ions should contribute to $A_g + 2B_g + A_u + 2B_u$, $A_g + 2B_g + A_u + 2B_u$ and $3A_g + 3B_g + 3A_u + 3B_u$ modes, respectively. It should be remembered, however, that three of these translational motions, $A_u + 2B_u$, correspond to acoustic modes. Vibrations of the oxygen ions contribute to $12A_g + 12B_g + 12A_u + 12B_u$ modes. These modes involve stretching and bending vibrations of the W–O bonds as well as librations of the tungsten–oxygen polyhedra. In the literature, the assignment of modes for this family of compounds was proposed based on three different approaches. Pujol et al. assigned the observed modes assuming that the main building units are $WO_4$ tetrahedra, which are however strongly distorted due to significant interactions via the double and single oxygen bridges [2]. On the other hand, Zhao et al. assumed that the structure is built up from $WO_6$ octahedra and they classified the modes according to stretching ($\nu_1$, $\nu_2$ and $\nu_3$) and bending ($\nu_4$, $\nu_5$ and $\nu_6$) modes of the $WO_6$ unit [3]. The both approaches are significantly simplified since the interactions between the $WO_4$ units are relatively strong and they cannot be treated as isolated units. On the other hand, the $WO_6$ ocatehdra are also not typical since some W–O distances are very large. For instance, for $RbNd(WO_4)_2$ the longest distance is 2.347 Å [8]. Therefore, we have previously proposed that for this family of compounds the bands should be assigned taking into account that the structure contains both short W–O bonds, which do not participate in formation of oxygen bridges, as well as double and single oxygen bridges [9–12]. In the present paper, we will assign the modes based on this latter approach.

The recorded Raman and IR spectra are presented in Figs. 1 and 2. The IR reflection spectra, presented in Fig. 2, were fitted by using four parameters model [16] in order to give information about TO and LO wavenumbers. According to this model, the complex dielectric constant is expressed in terms of the IR-active modes as follows:

$$\varepsilon(\omega) = \varepsilon_\infty \prod_j \frac{\omega_{jLO}^2 - \omega^2 + i\omega\gamma_{jLO}}{\omega_{jTO}^2 - \omega^2 + i\omega\gamma_{jTO}} \quad (1)$$

where $\omega_{jTO}$ and $\omega_{jLO}$ correspond to the resonance wavenumbers of the jth transversal and longitudinal modes, respectively, and $\gamma_{jTO}$ and $\gamma_{jLO}$ are the corresponding damping factors. $\varepsilon_\infty$ is the dielectric constant. For normal incidence, the infrared reflectivity $R$ and the dielectric function are related by:

$$R = \left| \frac{\sqrt{\varepsilon} - 1}{\sqrt{\varepsilon} + 1} \right|^2 \quad (2)$$

The results of fitting of the experimental data to the four-parameter model are shown in Fig. 3 and Table 1, and Raman wavenumbers are listed in Table 2.