

FTIR absorption study of hydroxyl ions in $\text{KHo}(\text{WO}_4)_2$ single crystals

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The presence of hydroxyl ions has been detected in as-grown $\text{KHo}(\text{WO}_4)_2$ double tungstate single crystals by Fourier Transform Infrared (FTIR) spectroscopy. The absorption bands of the stretching vibration of OH^- ions have been observed between 8–300 K in the 3450–3650 cm^{-1} wave number range. The temperature and polarization dependences of several intense narrow absorption lines corresponding to hydroxyl ions in different environments have been studied in detail. All lines were shifted, broadened and their intensity was decreased by increasing temperature due to phonon coupling. The band intensities strongly depended on the light propagation and polarization directions, allowing the determination of the orientation of OH^- dipoles with respect to the crystallographic axes. The isotopic replicas of several OH^- bands have been detected between 2550–2650 cm^{-1} in crystals treated in D_2O water vapour at 873 K.

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1 Introduction

Potassium holmium double tungstate, $\text{KHo}(\text{WO}_4)_2$, belongs to the family of alkali metal rare-earth double tungstates with promising applications as a laser material and as a cooling agent in adiabatic demagnetization for obtaining very low temperatures. High quality single crystals have recently been grown by high temperature solution growth methods [1–3]. $\text{KHo}(\text{WO}_4)_2$ crystallizes in monoclinic structure characterized by the space group $C2/c$. The optical absorption and luminescence properties of $\text{KHo}(\text{WO}_4)_2$ related to the electronic transitions of Ho^{3+} ions have been studied in wide frequency and temperature ranges [1–4].

The optical properties of many oxides are influenced by the presence of hydroxyl ions in the crystals. Oxide crystals grown by the Czochralski or top-seeded solution growth methods in air often incorporate OH^- ions [5]. The frequency of the stretching vibration of hydroxyl ions falls in the 3200–3700 cm^{-1} range where the electronic transitions of several rare-earth ions can also be detected. The aim of the present paper is to study the transmittance of $\text{KHo}(\text{WO}_4)_2$ crystal in this wave number range and to identify and characterize the absorption bands observed.

2 Experimental

$\text{KHo}(\text{WO}_4)_2$ crystals were grown by the top-seeded solution growth method described elsewhere [3]. The samples were oriented by X-ray diffraction and thin plates parallel to the ac and bc planes were prepared. The absorption spectra of the crystals were recorded by FTIR spectroscopy using a Bomem DA8 and a Bruker

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IFS66v/s high resolution spectrometer. Typical apodized resolution was between 0.05–0.2 cm^{-1} . The spectra were recorded in the 8–300 K temperature range by placing the samples in a closed-cycle helium cryostat of CTI-Cryogenics. Polarization dependence measurements were performed by using a wire grid polarizer deposited on KRS-5 window.

3 Results and discussion

The absorption spectra of an as-grown $\text{KHo}(\text{WO}_4)_2$ crystal are shown in Fig. 1. Unpolarized light was propagating along the b axis of the crystal. Two overlapping bands around $\nu = 3520\text{--}3530 \text{ cm}^{-1}$ and two very weak lines at about 3460 and 3470 cm^{-1} can be seen at 300 K. By lowering the temperature to 160 K the overlapping bands split and the small features at lower wave numbers become more pronounced. At 50 K additional bands appear above 3550 cm^{-1} . Further increase of the line intensities and narrowing of the halfwidths were observed at 9 K. The full width at half maximum ($\Delta\nu$) for some of the lines was as low as about 0.5 cm^{-1} at this temperature.

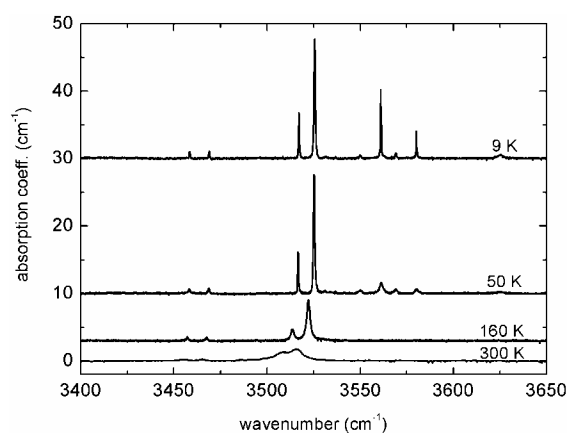


Fig. 1 Absorption bands for unpolarized light propagating along the b axis of an as-grown $\text{KHo}(\text{WO}_4)_2$ crystal in the 3400–3650 cm^{-1} wave number range between 9–300 K.

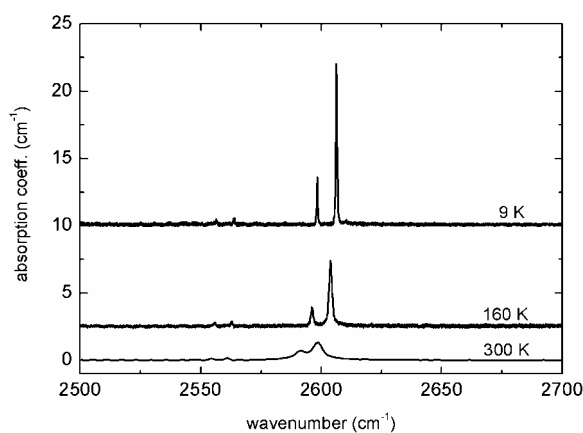


Fig. 2 Absorption spectra of $\text{KHo}(\text{WO}_4)_2$ in the 2500–2700 cm^{-1} wave number range measured after a heat treatment of the sample at D_2O vapour atmosphere.

Table 1 OH^- and OD^- band parameters in $\text{KHo}(\text{WO}_4)_2$ measured at 8 K (ω_e is the harmonic frequency, x_e is the anharmonicity parameter calculated from the anharmonic potential model).

$\nu_{\text{OH}} (\text{cm}^{-1})$	$\Delta\nu_{\text{OH}} (\text{cm}^{-1})$	$\nu_{\text{OD}} (\text{cm}^{-1})$	$\omega_e (\text{cm}^{-1})$	x_e
3458.86 w	0.64	2556.55	3653.1	0.02659
3469.16 w	0.61	2563.86	3662.5	0.02639
3517.31 s	0.51	2598.39	3707.9	0.02570
3525.75 s	0.82	2606.34	3725.5	0.02681
3550.00 w	1.2	-	-	-
3560.96 s	0.44	-	-	-
3569.03 w	0.7	-	-	-
3580.07 s	0.41	-	-	-
3625.09 w	3.9	-	-	-

The absorption bands in the 3400–3650 cm^{-1} wave number range can be tentatively attributed to the 0→1 transition of the stretching vibration of OH^- ions. Similar bands related to hydroxyl ions have been observed in many oxide crystals with different structures like perovskites, sillenites, garnets, etc. [5]. OH^- bands have also been detected in pure and doped ZnWO_4 [6,7] and CdWO_4 [8], but, to our knowledge, the presence of hydroxyl ions in double tungstates has not been reported so far.

The presence of OH^- bands can be justified by the isotopic exchange process. High temperature treatments in heavy water vapour atmosphere generally result in the appearance of OD^- bands in the crystals. Our $\text{KHo}(\text{WO}_4)_2$ crystal was heated to 873 K for one hour in air bubbled through D_2O and then the absorption spectrum was measured again at low temperature. Fig. 2 shows the spectra in the 2500–2700 cm^{-1} wave number range where the isotopic replica of the hydroxyl bands appeared. The similarity of the OH^- and OD^- spectra in the low wave number region is obvious for all temperatures, but OD^- bands corresponding to the OH^- bands above 3550 cm^{-1} are missing. This may be related to the different stability of the OH^- defects at the temperature of the heat treatment.

The parameters of the anharmonic vibrational potential of the hydroxyl ion can be calculated from the OH^- and OD^- stretching frequencies (see the relevant equations e.g. in ref. [5]). The x_e anharmonicity coefficients shown in Table 1 are in excellent agreement with those found for hydroxyl ions in other oxide crystals [5]. No significant change of x_e was observed as a function of temperature.

The coupling of the OH^- vibration to lattice phonons results in a characteristic temperature dependence of the band parameters, see e.g. in ref. [5]. The vibrational frequency shifts, the halfwidth broadens and the intensity decreases with increasing temperature. The same general tendencies are observed for the OH^- bands in $\text{KHo}(\text{WO}_4)_2$ crystal, although significant differences between the bands are seen. The temperature dependence of the band position, halfwidth and intensity are shown in Fig. 3 for the four most intense bands in $\text{KHo}(\text{WO}_4)_2$ crystal. Two of them (at about 3517 cm^{-1} and 3525 cm^{-1} at 8 K) shift to lower energies, while the other two (at about 3561 cm^{-1} and 3580 cm^{-1} at 8 K) slightly shift to higher energies for increasing temperature (Fig. 3a). The latter two bands broaden unusually rapidly (Fig. 3c) and disappear above 80 K (Fig. 3b). Applying the model of weak coupling of a single phonon band one can determine the frequency of the coupled phonon [5]. In the case of the latter bands the condition of weak coupling ($|\delta\omega| \ll \gamma$) was not fulfilled. Therefore the model cannot be regarded to be valid. For the other two bands the obtained phonon frequencies agree quite well with those determined by IR and Raman spectroscopic methods [9], see Table 2. It has to be emphasized, however, that the band intensities showed an anomalous behaviour below 50 K (see Fig. 3b), which makes the fitting of the phonon coupling model uncertain, at least at low temperatures, and indicates a possible structural phase transition in the crystal. Such a phase transition has been observed in a series of alkali metal double tungstates and molybdates [10].

Table 2 Parameters of the model of weak coupling of a single phonon band ($\delta\omega$ is the coupling constant, ω_o is the phonon frequency, γ is the phonon band width).

ν_o (cm^{-1})	$\Delta\nu_o$ (cm^{-1})	$\delta\omega$	ω_o (cm^{-1})	γ (cm^{-1})
3516.9 ± 0.34	0.45 ± 0.41	-6.6 ± 8.9	$121 \pm 106^*$	37 ± 35
3525.3 ± 0.35	0.74 ± 0.40	-13.7 ± 8.9	$185 \pm 76^*$	61 ± 28
3560.9 ± 0.37	0.53 ± 0.47	$0.9 \pm 4.0^{**}$	40 ± 111	$1 \pm 3^{**}$
3580.0 ± 0.16	0.64 ± 0.48	$2.2 \pm 8.8^{**}$	137 ± 85	$0.2 \pm 1.6^{**}$

*In agreement with Raman and IR frequencies [9]; **Weak coupling condition is not fulfilled.

Table 3 Directions of the OH^- dipole moments, χ_1 and χ_2 with respect to the optical indicatrix axes, X and Y, in the ac and bc planes, respectively.

ν_{OH} at 8 K (cm^{-1})	χ_1 ($^\circ$)	χ_2 ($^\circ$)
3517	73	23
3525	54	43
3561	30	25
3580	17	23

The polarization dependence of the OH^- absorption was also measured on samples cut parallel to the ac and bc planes. The band intensities changed remarkably for all bands when the light polarization was rotated with respect to the crystallographic axes of the crystal. Absorption maxima and minima appeared for light polarized along the axes of the optical indicatrix (see Fig. 4). From the ratio of the band intensities at the maxima and minima ($A_{\text{max}}/A_{\text{min}} \approx \cot^2\chi$) one can calculate the angle χ between the projection of the OH^- dipole onto the plane perpendicular to the propagation direction and the axes of the indicatrix (see Table 3).

Table 3 demonstrates that the four main OH⁻ bands show different polarization dependences indicating different dipole moment directions with respect to the crystallographic axes. Assuming that the OH⁻ ion substituting for an oxygen in the lattice vibrates along O–O bonds, one can find correspondence between the direction of the dipole moments and the O–O bonds of the different distorted polyhedra (octahedra, dodecahedra and icosahedra around W, Ho and K ions, respectively). Such a comparison is under way and will be published elsewhere. It may result in the determination of the exact positions of the hydrogen in the lattice.

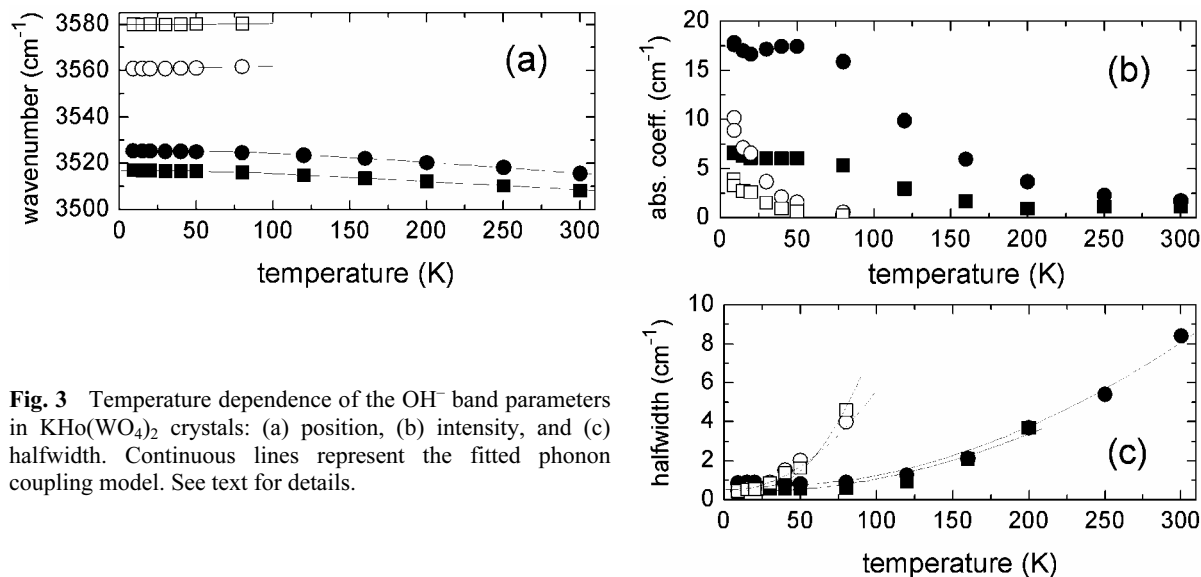


Fig. 3 Temperature dependence of the OH⁻ band parameters in KHo(WO₄)₂ crystals: (a) position, (b) intensity, and (c) halfwidth. Continuous lines represent the fitted phonon coupling model. See text for details.

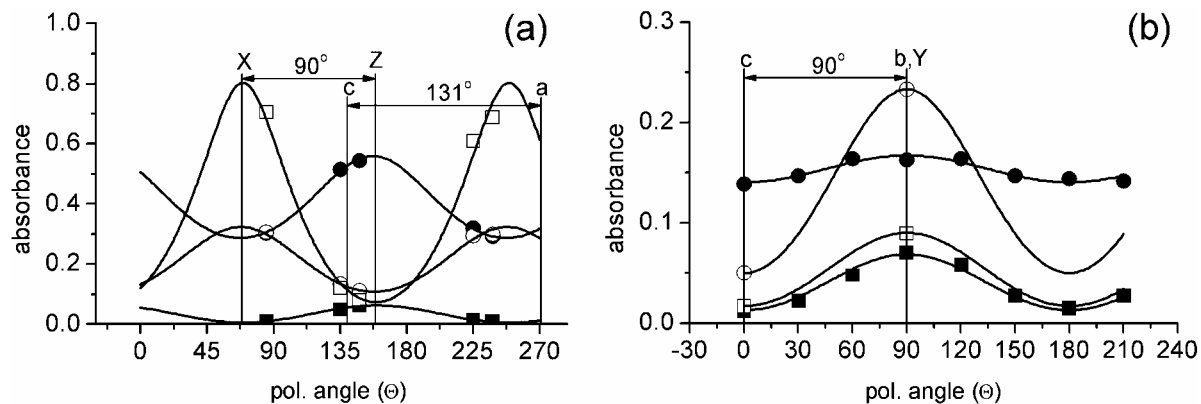


Fig. 4 Polarization dependence of the four main OH⁻ bands in KHo(WO₄)₂ (symbols represent the corresponding bands shown in Fig. 3a). X, Y, Z and a, b, c are the axes of the optical indicatrix and the crystallographic axes, respectively; (a) light propagates perpendicular to the ac plane, along b ≡ Y, (b) light propagates perpendicular to the bc plane. Continuous lines were fitted according to the equation given e.g. in ref. [5].

4 Conclusions

The presence of hydroxyl ions (OH⁻) has been detected in as-grown KHo(WO₄)₂ crystals by high resolution FTIR absorption spectroscopy. The anharmonicity of OH⁻ stretching mode measured after isotopic substitution is in agreement with that found in other oxide crystals. An anomalous behaviour of the band parameters has been observed below 50 K, indicating possible structural phase transition. The temperature dependence of the 3517 cm⁻¹ and 3525 cm⁻¹ bands has been interpreted by weak single phonon coupling. OH⁻ dipoles are located along the different O–O bonds of the distorted polyhedra.

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