Polarised infrared and Raman studies of YCa$_4$O(BO$_3$)$_3$

a non-linear optical single crystal

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Abstract

YCa$_4$(BO$_3$)$_3$-(YCOB) is a non-linear optical (NLO) material grown by Czochralski technique. Polarised IR, ATR–IR, polarised Raman and optical transmission spectral measurements were made. A series of absorption bands have been observed with intensities depending on the functional groups of the crystals. The observed bands were assigned and discussed.

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1. Introduction

The overwhelming success of molecular engineering in controlling non-linear optical properties has promoted the growth and characterization of variety of new types of non-linear optical materials (NLO). These materials are capable of generating efficient second harmonics. NLO crystals allow the production of coherent light beams in a wide range of wavelengths. When pumped with laser radiations of frequencies $\nu_1$ and $\nu_2$, NLO materials may generate beams at $2\nu_1$ and $2\nu_2$ (second harmonic generation, SHG), $\nu_1 + \nu_2$ and $\nu_1 - \nu_2$ (sum and difference frequency mixing SFM and DFM). Furthermore through optical parametric oscillations (OPO effect), it is possible with an NLO crystal to split an incident laser beam into two tunable beams whose photon energies sum is equal to the energy of pump photon [1].

Yttrium calcium oxo borate YCa$_4$O(BO$_3$)$_3$-(YCOB) is an excellent non-linear optical crystal. It has relatively a large second order NLO susceptibility, high laser damage threshold and wide transparency range in the UV region. YCOB is a phase matchable for the third harmonic generation of Nd: YAG laser [2]. The NLO applications of YCOB crystals were studied by Sasaki and co-workers [3] and Chai et al [4,5].

In order to understand the vibrational spectral properties of YCOB, in the present study an attempt has been made to grow YCOB crystal by conventional Czochralski technique and the IR absorption, Raman and optical transmission spectra were measured and discussed in detail.

2. Experimental details

2.1. Crystal growth

YCOB powder was prepared by solid state reaction at 1510°C from an intimate mixture of Y$_2$O$_3$, CaCO$_3$ and H$_3$BO$_3$ in appropriate proportions. Single crystals of YCOB upto 1 cm diameter by 3 cm in length were grown by conventional Czochralski technique. The typical pull and rotation were 3 mm/h and 20 rpm, respectively.

YCOB belongs to monoclinic (Cm space group) structure. There are two kinds of isolated (BO$_3$)$^-$ groups. They lie in planes perpendicular to [010] for one group and are skewed by $\sim$30° for the other. There are also two types of distorted octahedral Ca$^{2+}$ sites and Y$^{3+}$ ions are located in the mirror plane of the monoclinic structure, in six-fold coordination with C$_2$ site symmetry. The crystal structure and the photograph of YCOB [as grown] crystal are shown in Fig. 1a and b, respectively. Table 1 presents the summary of some basic properties of YCOB [6].
2.2. Recording of spectra

2.2.1. Polarised IR measurements

Polarised IR absorption spectra were recorded on Thermo Nicolet Magna 750 spectrophotometer. For this experiment, a Specac wire grid polariser at room temperature on KRS-5 substrate having about 95% degree of polarisation at 3 μm was used. The polarised IR spectra for 0 and 90° polarisation geometries were measured in the region 600–1600 cm⁻¹ with the electric vector parallel to X-, Y- and Z-directions (optical) of the crystal.

2.2.2. ATR–IR measurements

Attenuated total reflection (ATR) spectroscopy is a versatile and powerful technique for infrared sampling, since materials are normally analysed by ATR with minimal or no sample preparation. It is a rapid technique for obtaining the infrared spectrum of a material. Materials which are either too thick or too strongly absorbing to be analysed by transmission spectroscopy can be routinely analysed using ATR spectroscopy. ATR is also useful when only the surface of the material is of interest.

Internal reflection spectroscopy is a common infrared technique in which the infrared radiation is passed through an infrared transmitting crystal of high refractive index (ZnSe or Ge) allowing the radiation to reflect in the crystal one or more times. In this way, an evanescent wave penetrates into the sample in contact with the crystal producing a spectrum of the sample. In the most common application of this technique, the sampling surface is held in vertical orientation, with the sample material placed on one or both sides of the ATR crystal. The following equation defines the effective path length (EPL) for the single/multibounce. These calculations can be used to determine the best crystal materials for specific applications.

\[
EPL = \frac{\text{Number of reflections} \times \text{depth of penetration}}{(dP)}
\]

where \( \lambda \) is the wavelength (cm⁻¹), \( n_1 \) the refractive index of crystal [ZnSe or Ge], \( n_s \) the refractive index of sample, \( \theta \) is the crystal face angle [degrees approximately 45° for this accessory]

ATR–FTIR measurements for YCOB crystal were recorded in the region 600–2000 cm⁻¹ at 2 cm⁻¹ resolution on a Nicolet Magna 750 FTIR spectrophotometer equipped with a DTGS detector.

The horizontal ATR element used in this measurement was a standard trapezoidal ZnSe crystal with dimensions of 72 mm x 10 mm x 6 mm and an angle of incidence of 45° giving 12 reflections in contact with YCOB crystal. The transmission range of the ATR crystal (ZnSe) used in this study is between 20,000–650 cm⁻¹. The refractive index and the density of the ZnSe ATR crystal is 2.4 and 5.27 g/cm³, respectively.

2.2.3. Polarised Raman measurements

The sample of YCOB for the Raman experiment was cut into the shape of a parallelopped. The crystallographic \( a \), \( b \) and \( c \) axes coincides with the X-, Y- and Z-directions (op-
Fig. 2. IR spectra for (a) 0° polarisation and (b) 90° polarisation.
tical), respectively. In order to study the polarisation dependence, the crystal was fixed on a plate and mounted on a goniometer head. The analyser was placed before the elliptical mirror. The polarisation scrambler was placed before the entrance slit. The rotation of polarisation of laser beam is achieved by placing 90° polarisation rotator in front of lasermate. The spectra were measured in the region 100–1700 cm⁻¹ at 2 cm⁻¹ resolution by means of a Nicolet 950 FT Raman instrument equipped with a liquid N₂ cooled Ge detector using 1064 nm line of a Nd: YAG laser at 150 mW output power for excitation.

3. Results and discussion

3.1. Spectral analysis

The room temperature polarised IR spectra recorded along the electric vector parallel to X-, Y- and Z-directions for 0° and 90° polarisation geometries are shown in Fig. 2a and b, respectively. The ATR-IR spectrum of YCOB is presented in Fig. 3. The room temperature polarised Raman spectra of the sample are given in Fig. 4 for the scattering configurations X(YY)X, X(YZ)X and X(ZZ)X, respectively. The observed frequencies with their assignments are summarised in Table 2.

In the borate compounds containing (BO₃)³⁻ groups, the electronic delocalization in the planar borate anions is predominant and hence induce NLO properties (linked to their polarizability) as well as large birefringence (depending upon the relative orientation of the borate groups) required to fulfil the phase matching conditions [7]. Hence in the present study vibrations due to (BO₃)³⁻ groups have been discussed.

In the 0° polarised infrared absorption spectra, the ring B–O symmetric stretching vibrations were found at 786, 792 and 924 cm⁻¹ when E∥X. The bands with the similar frequencies and intensities were observed for E∥Z orientation also. However, in E∥X, the peaks corresponds to these vibrations were observed at 923 and 943 cm⁻¹.

In ATR-IR spectrum, the ring B–O symmetric stretching vibrations were observed at 792 and 936 cm⁻¹. In the polarised Raman spectra the B–O symmetric stretching vibrations were observed as doublets at 935 and 948 cm⁻¹ in X(YY)X, X(YZ)X and X(ZZ)X orientations, respectively. Even though the observed Raman shifts (cm⁻¹) for these orientations were found to be similar, a drastic change and twist were observed in the intensities of these doublets.

3.2. Optical transmission spectrum

The optical transmission spectrum was recorded using Varian Cary 5E UV-Vis–NIR spectrophotometer in the range 200–2000 nm with high resolution and it is shown in Fig. 5. YCOB was found to have low absorption at the Nd: YAG fundamental wavelength (1064 nm) which contributes to its resistance to laser induced damage. Also, there were very little absorptions at the doubled (532 nm) and the tripled (355 nm) wavelengths, which can improve

![Fig. 3. ATR-IR spectrum.](image-url)
Fig. 4. Polarised Raman spectra.

Fig. 5. Optical transmission spectrum of YCOB.
Table 2
Assignments of observed bands of YCa_4O(BO_3)_3

<table>
<thead>
<tr>
<th>Polarization</th>
<th>Infrared (cm(^{-1}))</th>
<th>ATR-IR (cm(^{-1}))</th>
<th>Raman (cm(^{-1}))</th>
<th>Assignments</th>
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<tr>
<td></td>
<td>Pol 0(^\circ)</td>
<td>Pol 90(^\circ)</td>
<td>X((\Gamma))</td>
<td>X((\Sigma))</td>
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vvw, Very very weak; vw, very weak; w, weak; m, medium; s, strong.
Fig. 6. Second harmonic green signal at 532 nm.

the second and third harmonic throughputs. The absorptions in the range 240–320 nm are due to $\text{Y}^{3+}$ ions of YCOB.

3.3. Second harmonic generation [SHG]

The SHG property of the as grown YCOB crystal is observed using a Q-switched Nd: YAG laser. The crystal is mounted on a crystal holder and infrared radiation ($\lambda = 1064 \text{ nm}$) is made to incident on the YCOB crystal from the Nd:YAG laser. The beam is well focussed. It is observed that the second harmonic green signal ($\lambda = 532 \text{ nm}$) is generated by the YCOB crystal in addition to the original infrared wavelength. Using a suitable dichroic mirror, infrared wavelength is filtered and the second harmonic green signal is recorded using a DIDA 512 G/R model fluorescence spectroscope. The wavelength is scanned with the aid of a monochromator in the spectroscope and it is presented in Fig. 6.

4. Conclusions

A satisfactory vibrational spectral data for YCa$_4$O(BO$_3$)$_3$, a non-linear optical single crystal has been made available through this study. The optical transmission study of YCOB reveals that the crystal has good transmission in the entire visible region. Owing to the good quality transparency, yttrium calcium oxoborate crystal seems to be a promising material for NLO applications. The NLO property of second harmonic generation has also been verified. Further studies on the improvement of the efficiency of SHG due to ion irradiation are in progress.

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References