POLARISED RAMAN STUDIES OF $YCa_4O(BO_3)_3$ – A NON – LINEAR OPTICAL SINGLE CRYSTAL

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Abstract: $YCa_4O(BO_3)_3$ - (YCOB) is a nonlinear optical (NLO) material grown by Czochralski technique. Polarised Raman spectral measurements were made. A series of bands have been observed with intensities depending on the functional groups of the crystals. The observed bands were assigned and discussed.

The overwhelming success of molecular engineering in controlling non-linear optical properties has promoted the growth and characterisation of variety of new types of nonlinear 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 ν_1 and ν_2, NLO materials may generate beams at $2\nu_1$ and $2\nu_2$ (SHG), $\nu_1 + \nu_2$ and $\nu_1 - \nu_2$ (sum and difference frequency mixing (SFM, 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.Yttrium calcium oxo borate $YCa_4O(BO_3)_3$ - (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. The NLO applications of YCOB crystals were studied by Sasaki et al [1] and Chai et al [2]. 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 polarised Raman spectra were measured and discussed in detail.YCOB powder was prepared by solid state reaction at 1510°C from an intimate mixture of Y_2O_3, $CaCO_3$ and H_3BO_3 in appropriate proportions. Single crystals of YCOB upto 1 cm diameter by 3 cm in length (Fig.1) were grown by conventional Czochralski technique. The typical pull and rotation were 3 mm /hr and 20 rpm respectively. YCOB belongs to monoclinic (Cm space group) structure. There are two kinds of isolated $(BO_3)^{3-}$ groups. They lie in planes perpendicular to [001] for one group and are skewed by ~ 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_s site symmetry. The Polarised Raman 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 - N_2 - cooled Ge detector using 1064 nm line of a Nd : YAG laser at 150 mw output power for excitation.

The room temperature polarised Raman spectra of the sample are given in Fig.2 for the scattering configurations $X(YY)\bar{X}$, $X(YZ)\bar{X}$ and $X(ZZ)\bar{X}$ respectively. In the borate compounds containing $(BO_3)^{3-}$ 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 fulfill the phase matching conditions. Hence in the present study vibrations due to $(BO_3)^{3-}$ groups have been discussed. In the polarised Raman

spectra the B-O symmetric stretching vibrations were observed as doublets at 935 and 948 cm^{-1} in $X(YY)\bar{X}$, $X(YZ)\bar{X}$ and $X(ZZ)\bar{X}$ orientations respectively. Eventhough 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. In $X(YY)\bar{X}$ geometry, the 935 cm^{-1} peak was found stronger and intense when compared to its 948 cm^{-1} counterpart. However in $X(YZ)\bar{X}$ orientation the intensity of the peaks were interchanged. That is, the intensity of the peak 935 cm^{-1} became low and 948 cm^{-1} became strong. In the $X(ZZ)\bar{X}$ orientation, the intensities of these doublets were drastically reduced. The phenomena observed in the polarised Raman spectra for YCOB crystal indicates that the crystal is a non-centro symmetric (otherwise its second order NLO susceptibility vanishes), which is an essential property for a crystal to exhibit non-linear optical activity [1]. A satisfactory vibrational spectral data for $YCa_4O(BO_3)_3$, a nonlinear optical single crystal has been made available through this study.

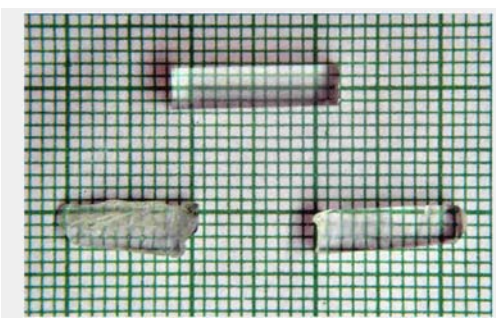

Fig.1. As grown YCOB

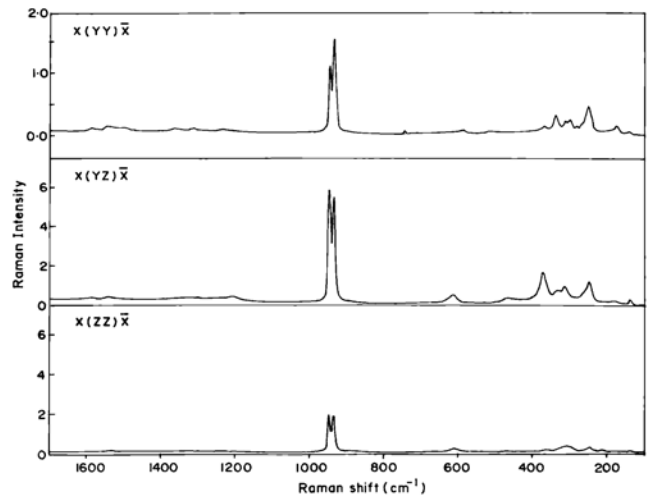

Fig.2. Polarised Raman spectra

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