Anisotropic crystal of the $\delta$-BiB$_3$O$_6$ investigated by vibrational spectroscopy

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Abstract. The vibrational spectroscopy has been applied to investigate the structure the BiB3O6 (BIBO) crystal. Based on the experimental results, the total set of phonons mode of the polarized Raman spectra was proposed. To verify the obtained experimental data have been performed theoretical calculation in software package LADY.

1. Introduction

BiB$_3$O$_6$ (BIBO) has excellent optical nonlinear properties for conversion frequency in the solid state lasers [1]. It is most effective in the optical range UV and visible light which have widely been used in medicine, signal progressing. BIBO have large nonlinear optical coefficient due to its structure and non-hydroscopic nature [2].

Long time thought that BiB$_3$O$_6$ have only alpha phase with space group symmetry C2. [3] Recently have been found new six phase of this compound. More extensively known and studied phase is $\alpha$-BiB$_3$O$_6$, which build from chain bounded triangles [BO$_3$] and tetrahedrons [BO$_4$] in range 1:2. $\beta$-BiB$_3$O$_6$ is metastable phase and it can undergo the phase transition in other phase at the high temperature. As $\alpha$ - BiB$_3$O$_6$, $\beta$ - BiB$_3$O$_6$ consist of chain bounded triangles [BO$_3$] and tetrahedrons [BO$_4$] in range 2:1. The first principles simulation showed that the main contribution in nonlinearity comes from [BO$_4$] tetrahedral units. Therefore, $\gamma$ and $\delta$ – BiB$_3$O$_6$ attract the great interest due to the features of their structures (Figure 1) which are exclusively consisting of the chains of bounded tetrahedrons [BO$_4$].

Figure 1. The crystal structure of $\delta$–BiB$_3$O$_6$. 
Since $\gamma$–BiB$_3$O$_6$ have inversion center, subject of the present research work is $\delta$–BiB$_3$O$_6$. The symmetry space group of orthorhombic $\delta$-phase is Pca$_2_1$ (Z=4). The expansion of the total vibrational representation in the Brillouin zone center for the $\delta$ phase has the following view: $\Gamma_{\text{Vibr}} = 30A_1 + 30A_2 + 30B_1 + 30B_2$, acoustic and optic modes: $\Gamma_{\text{acoustic}} = A_1 + B_1 + B_2$, $\Gamma_{\text{optic}} = 29A_1 + 30A_2 + 29B_1 + 29B_2$.

2. Experiment
The samples have been obtained same as described in the paper [4]. The assembling is spectrometer Horiba Jobin Yvon T64000 equipped with a liquid nitrogen cooled charge coupled device detection system in subtractive dispersion mode in 10 to 1600 cm$^{-1}$ range. The spectra were recorded in the backscattering geometry. It was used notation. [4]

3. Results and discussion
To simulate the $\delta$–BiB$_3$O$_6$ the vibrational spectrum package LADY was used. The program allows to obtain the full Raman spectrum using the model of ‘rigid-ion’. The interatomic potential is considered as a sum of the short-range interaction potentials was taken in the Born–Mayer form:

$$V^{\text{RM}}(r_{ij}) = \frac{1}{2} \sum_{j} \frac{Z_i Z_j}{r_{ij}} + U(r_{ij}),$$

and of the of long range Coulomb electrostatic potentials:

$$U(r_{ij}) = \lambda \exp(-r_{ij}/\rho),$$

where $r_{ij}$ is the interatomic distance and $\lambda$ and $\rho$ are the parameters characterizing of the short-range pair interionic interaction. Resulting model parameters were obtained by minimization of residual values of the simulated and experimental Raman frequencies using the Fletcher–Reeves method [5–7]. The values of $\lambda$, $\rho$ and $Z_{ij}$ are listed in Table 1.

| Interactions | Radii of interaction, Å | $\lambda$, aJ/Å$^2$ | $\rho$, Å |
|--------------|--------------------------|---------------------|-----------|
| Bi – O       | 0–3.00                   | 350.00              | 0.300     |
| B1 – O       | 0–1.50                   | 321.60              | 0.210     |
| B2 – O       | 0–1.60                   | 400.60              | 0.220     |
| B3 – O       | 0–1.60                   | 345.30              | 0.199     |
| O – O        | 0–3.00                   | 242.80              | 0.245     |
| Ion          | Bi                       | B                   | O         |
| $Z(e)$       | 2.00                     | 1.80                | -1.2333   |

The Raman active frequency is shown in Table 2 in comparison with experiment.
Table 2. The calculated Raman active frequencies are shown in Table 2 along with the experimental dates

|     | A₁  |     | A₂  |     | B₁  |     | B₂  |     |
|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| exp.| calc.| exp.| calc.| exp.| calc.| exp.| calc.|
| TO  | 1116| 1097| 1121| 1076| 1153| 1212| 1278|
| LO  | 1081| 1035| 1093| 1037| 1119| 1082| 1132| 1037| 1132|
|     | 1031| 1007| 979 | 1010| 1090| 1035| 1023| 1010| 1029|
|     | 996 | 975 | 959 | 978 | 981 | 997 | 949 | 997 | 965 |
|     | 959 | 935 | 908 | 944 | 945 | 955 | 938 | 956 | 929 |
|     | 919 | 907 | 894 | 905 | 912 | 919 | 910 | 936 | 905 |
|     | 864 | 865 | 789 | 864 | 805 | 897 | 854 | 880 | 892 |
|     | 807 | 783 | 752 | 784 | 755 | 863 | 803 | 784 | 786 |
|     | 783 | 727 | 721 | 728 | 751 | 813 | 749 | 727 | 737 |
|     | 752 | 650 | 697 | 709 | 730 | 783 | 732 | 665 | 689 |
|     | 726 | 607 | 634 | 607 | 648 | 753 | 648 | 607 | 647 |
|     | 639 | 530 | 598 | 558 | 606 | 727 | 618 | 515 | 623 |
|     | 606 | 515 | 552 | 534 | 553 | 607 | 575 | 499 | 563 |
|     | 530 | 502 | 510 | 514 | 529 | 578 | 533 | 468 | 518 |
|     | 499 | 467 | 490 | 501 | 511 | 531 | 504 | 415 | 483 |
|     | 467 | 416 | 447 | 466 | 490 | 515 | 497 | 393 | 459 |
|     | 415 | 394 | 428 | 417 | 428 | 500 | 432 | 327 | 442 |
|     | 393 | 329 | 384 | 393 | 416 | 467 | 421 | 312 | 400 |
|     | 328 | 310 | 345 | 330 | 382 | 415 | 392 | 304 | 383 |
|     | 303 | 256 | 320 | 313 | 332 | 394 | 347 | 249 | 338 |
|     | 272 | 244 | 274 | 255 | 310 | 327 | 319 | 226 | 307 |
|     | 228 | 235 | 255 | 246 | 262 | 304 | 299 | 204 | 280 |
|     | 186 | 225 | 221 | 226 | 227 | 245 | 267 | 185 | 240 |
|     | 175 | 194 | 159 | 196 | 191 | 229 | 229 | 177 | 185 |
|     | 122 | 165 | 128 | 126 | 170 | 184 | 156 | 166 | 135 |
|     | 97  | 120 | 100 | 110 | 94  | 123 | 116 | 123 | 119 |
|     | 71  | 88  | 69  | 89  | 89  | 116 | 89  | 112 | 94 |
|     | 67  | 69  | 46  | 68  | 70  | 97  | 76  | 98  | 66 |
|     | 46  | 49  | 18  | 51  | 54  | 71  | 55  | 69  | 35 |

Since the BO₄ bounded with B-O in crystal is not ideal we can observe a large number of vibrations in the range > 650 cm⁻¹. For this reason the whole spectrum is reached of lines. The simulations is shown that about 40 active modes appear in the range >650 cm⁻¹ for the different position of the polarization.

The bands below 150 cm⁻¹ are related with Bi translation vibrations. The lower wavenumber range of 150–350 cm⁻¹ contains translational, rotational and mixed vibrations of BO₄ tetrahedra. Bands in the 350–650 cm⁻¹ range are related with the distorted ν₂ and ν₄ BO₄ bending modes. Generally, frequency of ν₄ vibration should be above that of ν₂ vibration [8].
In the Figure 2 a,b is presented LO-TO splitting in depending on the different position of the polarization is presented. The lines corresponding to B\textsubscript{1} and B\textsubscript{2} modes are presented on Figure 3 a,b.

![Raman spectra](image)

**Figure 2.** Raman spectra of the $\delta$–BiB\textsubscript{3}O\textsubscript{6} crystal at: a) b(cc)b, b(aa)b, a(bb)a, a(cc)a b) c(aa)c, c(bb)c, c) c(ba)c, c(ab)c geometries
4. Conclusion

The polarization selection rules, lattice dynamic simulations and number of the spectral lines are in the good agreement with experiment. The full set of experimental Raman spectra polarizations is presented. The vibration modes are classified to corresponding Raman bands.

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