Temperature-dependent Raman spectroscopic study of bismuth borate $Bi_2ZnOB_2O_6$*

Zhang Ji(张 季)[a)†], Zhang De-Ming(张德明)[b)], Zhang Qing-Li(张庆礼)[b)], and Yin Shao-Tang(殷绍唐)[b)]

[a)] *Anhui Xin Hua University, Hefei* 230088, *China*

[b)] *Anhui Institute of Optics and Fine Mechanics, Chinese Academy of Sciences, Hefei* 230031, *China*

(Received 6 May 2014; revised manuscript received 15 July 2014; published online 25 November 2014)

A temperature-dependent Raman spectroscopic study on $Bi_2ZnOB_2O_6$ crystal was carried out to investigate the structure change of the crystal with the increase of temperature. Raman spectra of crystal $Bi_2ZnOB_2O_6$ were recorded in the spectral range 10–1600 cm^{-1} at room temperature first. Compared with the vibrational spectra of the referred compounds, satisfactory assignment of most of the high-energy modes to vibrations of Bi–O, B–O, and Zn–O bonds was achieved. In particular, the Raman high-frequency peak located at 1344 cm^{-1} was attributed to the B–O vibration in the BO_3 triangle. This temperature-dependent Raman spectroscopic study was carried out up to 600 °C. It was found that all the Raman lines exhibit decreases in frequency and the widths of the Raman peaks increase with increasing temperature. No phase transition was observed under 600 °C.

Keywords: $Bi_2ZnOB_2O_6$ crystal, high temperature Raman spectroscopy, vibrational mode

PACS: 78.30.–j, 81.70.–q, 63.70.+h **DOI:** 10.1088/1674-1056/24/1/017801

1. Introduction

The development of new crystals evokes a growing interest in synthesizing crystals with nonlinear optical (NLO) properties.[1–3] Binary bismuth borates, such as BiB_3O_6,[4,5] have been of enhanced interest due to their promising nonlinear optical properties[6–9] and large nonlinear optical susceptibilities.[10–15] A broad search for new NLO materials in the ternary ZnO–Bi_2O_3–B_2O_3 system leads to a new NLO crystal $Bi_2ZnOB_2O_6$ (BZB). The bismuth borate $Bi_2ZnB_2O_7$[16,17] was synthesized first by Barbier *et al.* using the solid-state reaction method in the temperature range 650–825 °C at 1 atm. Its structure has been determined by powder x-ray diffraction (XRD) and refined by the Rietveld method using powder neutron diffraction data.[18,19] In addition, a large single crystal of $Bi_2ZnOB_2O_6$ has been grown by the top-seeded growth method.[20,21] A high second harmonic generation (SHG) efficiency about 3–4 times that of KH_2PO_4 (KDP) and a wide SHG phase matching range make the BZB crystal a promising NLO material. However, the structural stabilization at high temperature is important to the NLO crystal as an optical device. Temperature-dependent Raman scattering measurements are well suited to obtain the structural information of the sample at different temperatures because of the dependence of the phonon modes on the temperature.[22,23]

$Bi_2ZnOB_2O_6$ belongs to the space group C_{2v}^8-*Pba*2 with four formula units in the primitive cell. The zone-center optical phonons can be classified according to the following irreducible representations: $\Gamma_{\rm opt} = 28A_1 + 41A_2 + 36B_1 + 36B_2$. The A_1, B_1, B_2 modes are both Raman and infrared active; and the A_2 mode is Raman active only. Polarized Raman scattering of BZB has been measured by Zhang *et al.*[24] In this work, we present a study of the Raman spectra of BZB and their dependence on the temperature. The temperature dependence of the Raman bands is studied to investigate the structural change of the crystal at high temperature.

2. Experiment

The $Bi_2ZnOB_2O_6$ polycrystalline powder was prepared by standard solid state reactions. ZnO, Bi_2O_3, and H_3BO_3 of analytic grade were mixed homogeneously with appropriate proportions in an agate mortar, and packed into a Pt crucible. The sample was heated slowly to 630 °C and held at this temperature for 48 h with several intermediate grindings and mixings. The analysis of x-ray powder diffraction shows that the final product is $Bi_2ZnOB_2O_6$.

The room- and high-temperature measurements were carried out using a home-made heating furnace. The temperature was monitored by a thermocouple attached to the metal sample holder and controlled by a temperature controller within 1 °C. The Raman spectra were collected with Horiba Jobin Y'von Raman spectrometer (LabRam800HR) with a backscattering configuration. The ultraviolet light pulse of 355 nm with a repetition frequency of 10 kHz from a Coherent Innova Ultra laser was focused onto the sample using a Raman microprobe with a 4× objective lens. An intensified charge coupled device (CCD) was used to collect the scattering light. The spectral acquisition, under the accumulated mode, was 10 s each for 10 times, the average power of the laser operation was fixed at

*Project supported by the National Natural Science Foundation of China (Grant Nos. 50932005 and 51102239).

†Corresponding author. E-mail: 18956063545@189.cn

© 2015 Chinese Physical Society and IOP Publishing Ltd

800 mW and the slit width was set at 300 nm for all the measurements under different temperatures.

3. Results and discussion

The structure of BZB is shown in Fig. 1. It has a three-dimensional network consisting of $ZnB_2O_7^{6-}$ layers connected through O–Bi–O bands along the *c* axis. In this structure, through sharing the O atoms, two $[BO_3]^{3-}$ triangles are condensed into a $[B_2O_5]^{4-}$ group and two $[BO_4]^{5-}$ tetrahedra are condensed into a $[B_2O_7]^{8-}$ group. The $[B_2O_5]^{4-}$ and $[B_2O_7]^{8-}$ groups are bridged by tetrahedral Zn^{2+} centers through sharing three O vertices of each $[ZnO_4]^{6-}$ tetrahedron to generate a 2D infinite $[ZnB_2O_7]^{6+}$ layer parallel to the (001) plane. Figure 2 shows the crystal Raman spectra in the range from 100 cm^{-1} to 1600 cm^{-1} at room temperature.

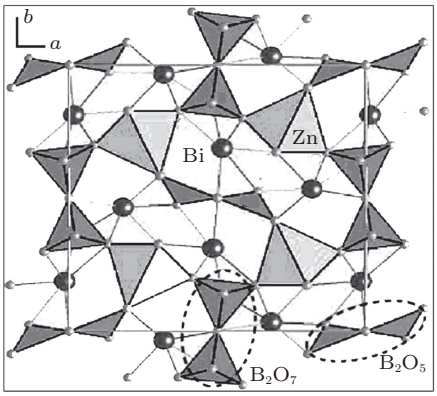


Fig. 1. Structure of $Bi_2ZnOB_2O_6$ viewed down the *c* axis.

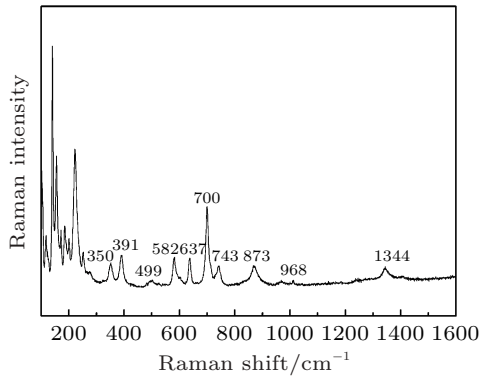


Fig. 2. Raman spectrum of $Bi_2ZnOB_2O_6$ crystal at room temperature.

In the structure of BZB, six-coordinated bismuth and the oxygens around form a distorted octahedron. Baia *et al.* assigned the Raman peaks located at 200–550 cm^{-1} and 880 cm^{-1} in the Raman spectrum of B_2O_3–Bi_2O_3 glasses to the Bi–O vibration.[25] The Raman peak at 350 cm^{-1} was observed in the Raman spectrum of B_2O_3–ZnO–Bi_2O_3 glasses due to the Bi–O–Bi vibration.[26] Therefore, the Raman peaks located at 350 cm^{-1} and 873 cm^{-1} are attributed to the Bi–O band of BiO_6 octahedra.

A significant contribution to the Raman spectra of BZB comes from the vibration of the low-symmetric polyborate $[B_2O_7]$ group with two BO_4 tetrahedra and the $[B_2O_5]$ group consisting of two BO_3 triangles. A planar equilateral triangle molecule XY_3 with symmetry D_{3h} has four normal vibrational modes. For the $[BO_3]$ group with symmetry D_{3h}, the ν_s mode represents a non-degenerate symmetric B–O stretching vibration, the δ mode represents a non-degenerate out-of-plane B–O bending vibration, the ν_{as} mode represents a doubly degenerate B–O stretching vibration, and the γ mode represents a doubly degenerate in-plane O–B–O bending vibration. It is known from the literature that the normal mode frequencies of the $[BO_3]$ group in the vibrational spectra of the bismuth borate crystals are typically situated as follows:[27,28] $\nu_s \sim 950$ cm^{-1}, $\delta \sim 650$–800 cm^{-1}, $\nu_{as} \sim 1100$–1450 cm^{-1}, and $\gamma \sim 500$–650 cm^{-1}. In the Raman spectra of the BZB crystal, the peaks at 700 cm^{-1} and 743 cm^{-1} are assigned to the bending vibration of the B–O bands, while the peak at 1344 cm^{-1} is assigned to the B–O stretching vibration. On the other hand, a tetrahedron molecule XY_4 with symmetry T_d has four normal vibrational modes: v_1 (symmetric stretching mode), v_2 (bending mode), v_3 (asymmetric stretching mode), and v_4 (bending mode). For the BO_4 tetrahedron, $v_1 \sim 800$–955 cm^{-1}, $v_2 \sim 400$–600 cm^{-1}, $v_3 \sim 1000$ cm^{-1}, and $v_4 \sim 600$ cm^{-1}.[29,30] Here the Raman peaks located at 637 cm^{-1} and 968 cm^{-1} are attributed to the B–O bond of the BO_4 tetrahedron. The Zn atoms as a bridge connect the boron–oxygen groups with Zn–O bonds. The Raman peaks at 380 cm^{-1} and 583 cm^{-1} were observed in the Raman spectrum of the ZnO crystal.[31,32] The Raman peaks at 328 cm^{-1}, 380 cm^{-1}, and 435 cm^{-1} were present in the Raman spectra of the polycrystalline $Zn_{1-x}Mg_xO$ ($x = 0$–0.15) powders, which were attributed to the Zn–O vibration.[33] Here, the Raman peaks located at 350 cm^{-1}, 391 cm^{-1}, and 582 cm^{-1} are related to the Zn–O bond vibration in the BZB crystal.

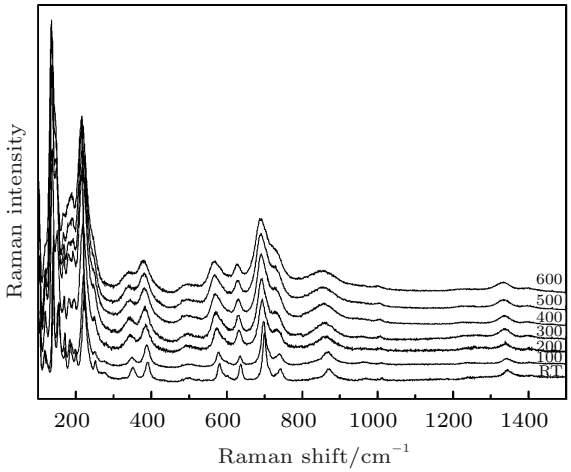


Fig. 3. Temperature dependent Raman spectra of $Bi_2ZnOB_2O_6$ crystal from room temperature to 600 °C.

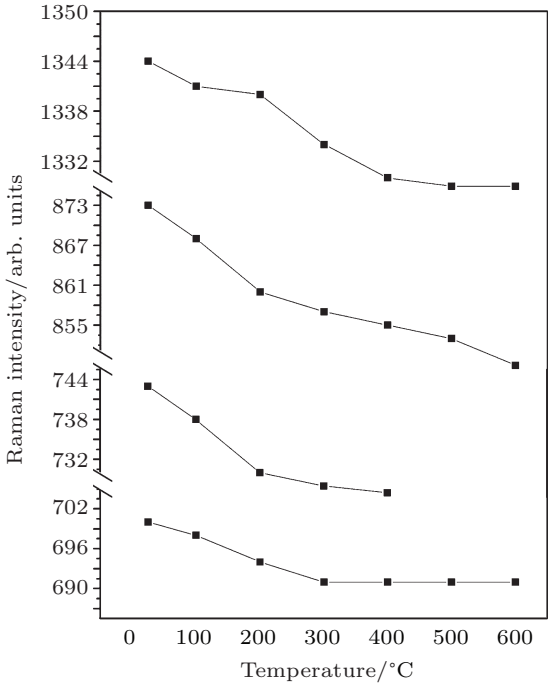


Fig. 4. The wavenumber shifts of Raman peaks at 1344 cm^{-1}, 873 cm^{-1}, 743 cm^{-1}, and 700 cm^{-1} with increasing temperature.

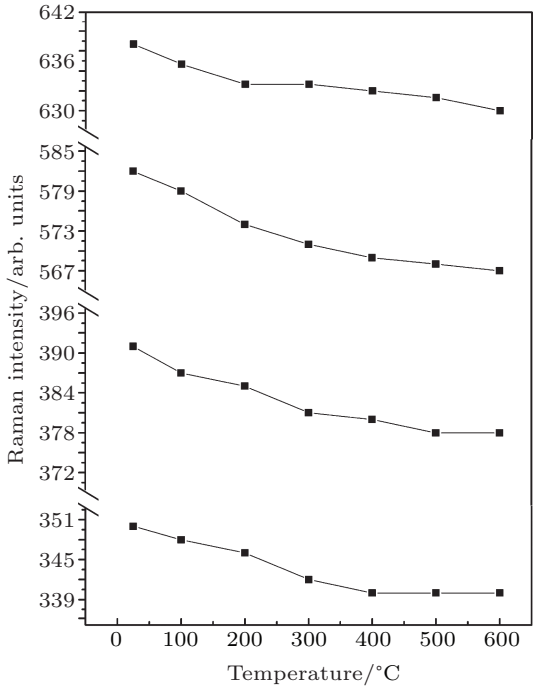


Fig. 5. The wavenumber shifts of Raman peaks at 637 cm^{-1}, 582 cm^{-1}, 391 cm^{-1}, and 350 cm^{-1} with increasing temperature.

The temperature dependent Raman spectra of a $Bi_2ZnOB_2O_6$ crystal with the wavenumber range from 100 cm^{-1} to 1600 cm^{-1} were recorded with increasing temperature from room temperature to 600 °C, as shown in Fig. 3. Nearly all the vibrational modes exhibit a decrease in wavenumber. Figures 4 and 5 illustrate the shifts of the Raman peaks with temperature. The Raman peaks located at 873 cm^{-1} and 1344 cm^{-1} have wavenumber shifts of 21 cm^{-1} and 15 cm^{-1}, respectively. These phenomena also appear in the high-temperature Raman spectra of $Bi_{12}SiO_{20}$, $KTa_{1-x}NbxO_3$, Ba_3 $(PO_4)_2$, and BiB_3O_6 crystals.[34–37] With increasing temperature, all of the peaks decrease in frequency, which is ascribed to the increases in the inter-atomic distances in the BZB crystal when the crystal is heated.[38] In addition, the Raman peaks become wider during the heating process, the bending vibration of the B–O bands at 743 cm^{-1} becomes a shoulder at 700 cm^{-1} after the temperature increases to 400 °C, as a consequence of larger distributions of the bonding angles and distances at higher temperature. Some of the adjacent peaks located below 300 cm^{-1} become overlapped and merge together with increasing temperature. However, the spectra of the $Bi_2ZnOB_2O_6$ crystal do not show any splitting or new bands, which indicates that no phase transition occurs in the present study.

4. Conclusion

A temperature-dependent Raman spectroscopic study on the $Bi_2ZnOB_2O_6$ crystal was carried out up to 600 °C. Raman spectra of single crystal $Bi_2ZnOB_2O_6$ were recorded in the spectral range 10–1600 cm^{-1} at room temperature first. Compared with the vibrational spectra of the referred compounds, satisfactory assignment of most of the high-energy modes to vibrations of Bi–O, B–O, and Zn–O bonds was achieved. In particular, the Raman high-frequency peak located at 1344 cm^{-1} was attributed to the B–O vibration in the $[BO_3]$ triangle. The changes of the Raman peaks and the crystal structure were investigated at high temperature. It was found that all the Raman peaks exhibit decreases in frequency and the widths of the Raman peaks increase with increasing temperature. No phase transition was observed under 600 °C.

Acknowledgement

The authors thank the High Magnetic Field Laboratory of the Chinese Academy of Sciences for providing the Raman spectrometer.

References

[1] Reshak A H, Chen X, Auluck S and Kityk I V 2008 *J. Chem. Phys.* **129** 204111
[2] Reshak A H and Auluck S 2007 *Physica B* **393** 88
[3] Reshak A H and Auluck S 2007 *Physica B* **388** 34
[4] Reshak A H, Kityk I V and Auluck S 2008 *Appl. Phys. A* **91** 451
[5] Reshak A H, Chen X and Auluck S 2009 *Jpn. J. Appl. Phys.* **48** 011601
[6] Becker P and Frohlich R Z 2004 *Naturforsch B* **59** 256
[7] Filatov S, Shepelev Y, Bubnova R, Sennova N, Egorysheva A V and Kargin Y F 2004 *J. Solid State Chem.* **177** 515
[8] Egorysheva A V, Kanishcheva A S, Kargin Y F, Gorbunova Y E and Mikhailov Y N 2002 *Zh. Neorg. Khim.* **47** 1961
[9] Muehlberg M, Burianek M, Edongue H and Poetsch C 2002 *J. Cryst. Growth* **740** 237
[10] Becker P, Liebertz J and Bohaty L 1999 *J. Cryst. Growth* **203** 149
[11] Kaminskii A, Becker P, Bohaty L, Ueda K, Takaichi K and Hanuza 2002 *J. Opt. Commun.* **206** 179
[12] Hellwig H, Liebertz J and Bohaty L 1999 *Solid State Commun.* **109** 249
[13] Lin Z, Wang Z, Chen C and Lee M H 2001 *J. Appl. Phys.* **90** 5585

[14] Teng B, Wang J, Wang Z, Hu X, Jiang H and Liu H 2001 *J. Cryst. Growth* **233** 282
[15] Teng B, Wang J, Wang Z, Jiang H and Hu X 2001 *J. Cryst. Growth* **224** 280
[16] Reshak A H, Chen X, Kityk I V and Auluck S 2007 *Curr. Opin. Solid State Mater. Sci.* **11** 33
[17] Reshak A H, Chen X, Kityk I V, Auluck S, Iliopoulos K, Couris S and Khenata R 2009 *Curr. Opin. Solid State Mater. Sci.* **12** 26
[18] Barbier J, Penin N and Cranswick L M 2005 *Chem. Mater.* **17** 3130
[19] Zhang Y, Wang W N and Wang G 2011 *Chin. Phys. B* **20** 123301
[20] Li F, Pan S L, Hou X L and Yao 2009 *J. Cryst. Growth* **9** 4091
[21] Li F, Hou X L, Pan S L and Wang X A 2009 *Chem. Mater.* **21** 2846
[22] Pereira K, Silva D, Santos J, Maczka M, Paraguassu W, Freire P T, Mendes Filho J and Hanuza J 2013 *J. Solid State Chem.* **199** 7
[23] Calizo I, Balandin A A, Bao W, Miao F and Lau C N 2007 *Nano Lett.* **7** 2645
[24] Zhang J, Zhang D M, Wang D, Zhang Q L, Sun D L and Yin S T 2013 *Acta Phys. Sin.* **62** 237802 (in Chinese)
[25] Baia L, Stefan R, Kiefer W and Simon S 2005 *J. Raman Spectrosc.* **36** 262
[26] Inoue T, Honmaa T, Dimitrov V and Komatsu T 2010 *J. Solid State Chem.* **183** 3078
[27] Weir C E, Schroeder R A. 1964 *J. Res. Sect. A* **68** 465
[28] Paul G L and Taylor W 1956 *J. Phys.* **25** 1184
[29] Steele W C and Decius J C 1956 *J. Chem. Phys.* **25** 1184
[30] Zhang J, Wang D, Zhang D M, Zhang Q L, Wan S M, Sun D L and Yin S T 2013 *Acta Phys. Sin.* **62** 037802 (in Chinese)
[31] Ma Y, Yang X H and Ye L J 2012 *Acta Phys. Sin.* **61** 247701 (in Chinese)
[32] Xu J F, Cheng G X and Du Y W 1996 *Chin. Phys. Lett.* **13** 765
[33] Young K, Katharine P, Andi M L, David R C and Ram S 2007 *Phys. Rev. B* **76** 115204
[34] Qiu H L, Wang A H, You J L, Liu X J, Chen H and Yin S T 2005 *Spectroscopy and Spectral Analysis* **25** 222 (in Chinese)
[35] Zhou W P, Wan S M, Yin S T Zhang Q L, You J L and Wang Y Y 2009 *Acta Phys. Sin.* **58** 0570 (in Chinese)
[36] Zhang J, Wang D, Zhang D M, Zhang Q L, Wan S M, Sun D L and Yin S T 2013 *Acta Phys. Sin.* **62** 097802 (in Chinese)
[37] Wan S M, Teng B, Zhang X, You J L, Zhou W P, Zhang Q L and Yin S T 2010 *CrystEngComm* **12** 211
[38] Cerderira F, Melo F E A and Lemos V 1983 *Phys. Rev. B* **27** 7716