High-temperature Raman spectroscopic study of vanadoborate $Na_3VO_2B_6O_{11}$*

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(Received 2 November 2015; revised manuscript received 13 December 2015; published online 18 January 2016)

Raman spectra of a vanadoborate ($Na_3VO_2B_6O_{11}$) crystal from room temperature up to the melting point have been recorded. The main internal vibrational modes of the crystal have been assigned. It was found that all the Raman bands exhibit decreases in frequency and the widths of the Raman bands increase with the increase of temperature. However, no phase transition was observed under 525 °C. The micro-structure of its melt was studied by quantum chemistry *ab initio* calculation. The continuous three-dimensional network of the crystal collapsed and transformed into VO_4 and VBO_6 clusters during the melting process with an isomerization reaction from four-coordinated boron to a three-coordinated species.

Keywords: $Na_3VO_2B_6O_{11}$ crystal, high-temperature Raman spectroscopy, vibration mode

PACS: 78.30.–j, 81.70.–q, 63.70.+h **DOI:** 10.1088/1674-1056/25/3/037802

1. Introduction

$Na_3VO_2B_6O_{11}$ (NVBO) is a new nonlinear optical crystal as a result of the investigation of vanadoborate systems. In the past years, $Na_2B_4O_7$–V_2O_5,[1] $NaBO_2$–V_2O_5,[2] and H_3BO_3–$NaVO_3$–HNO_3–H_2O[3] systems have been studied. More recently, Touboul *et al.*[4] further investigated the Na_2CO_3–H_2O–V_2O_5–H_3BO_3 system to obtain vanadoborate compound $Na_3VO_2B_6O_{11}$ first. Then the NVBO crystal has been grown by the top-seeded solution growth method using Na_2CO_3–V_2O_5 flux.[5] It has a wide transparency range from 370 nm to 3000 nm with the shortest second harmonic generation (SHG) wavelength at 427 nm, which demonstrates that it has potential as optical SHG crystals for blue wavelength applications.

The investigation of the structure of NVBO crystal by x-ray diffraction techniques shows that the compound is orthorhombic, space group $P2_12_12_1$,[4,5] with cell parameters $a = 7.7359$ Å, $b = 10.1884$ Å, $c = 12.5697$ Å, $V = 990.7$ Å, and $Z = 4$. It has a three-dimensional structure consisting of hexaborate groups connected by VO_4 tetrahedra with the sodium atoms distributed in channels throughout the three-dimensional network. Such a hexaborate group made up of a tetrahedron and triangle by sharing one oxygen may form compact atom groups which have been described in several borates, such as $Li_2B_4O_7$,[6] $CsLiB_6O_{10}$,[7] and LiB_3O_5[8] crystals. 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 temperature.[9,10] Furthermore, it is essential to investigate the micro-structure of both its crystal and molten phases for being able to achieve large-sized single crystals grown from the melt.[11] To the best of our knowledge, no studies on Raman scattering about the NVBO crystals have been reported until now, which contribute to a progressive understanding of the crystal structure[12] as well as more specific aspects of lattice dynamics.[13] Therefore, in this paper, we recorded the Raman spectra of NVBO single crystal from room temperature to melting point, and the calculation was carried out using quantum chemistry *ab initio* calculation to study the micro-structure of the solution.

2. Experiment

The NVBO single crystal used in this study was grown by the flux method in Na_2CO_3–V_2O_5 flux system described by Fan *et al.*[5] Then the crystal was cut into slices with 2-mm thickness. 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 sample was steadily heated from room temper-

*Project supported by the National Natural Science Foundation of China (Grant Nos. 51302268 and 51102239) and the Natural Science Foundation of Anhui Province, China (Grant No. KJ2015A339).

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ature to melting point in a platinum boat which was placed in the center of the chamber. The spectral acquisition, under the accumulated mode, was 10 s each time, the average power of the laser operation was fixed at 800 mW and the slit width was set as 300 nm for all the measurements under different temperatures.

3. Results and discussion

3.1. Structures and factor group analyses

The orthorhombic unit cell of the $Na_3VO_2B_6O_{11}$ crystal contains four formula units and belongs to the space groups $P2_12_12_1$. According to the research of Touboul,[4] two groups of atoms can be marked out in the structure of this compound: VO_4 and B_6O_{13} groups which share common oxygen atoms to form a three-dimensional framework, as shown in Fig. 1. The complex B_6O_{13} groups contain three non-planar six-member rings (which consist of one BO_3 triangle and two BO_4 tetrahedra, the mean values for B–O bonds are 1.367 Å and 1.469 Å, respectively, sharing with one oxygen. All atoms occupy Wyckoff positions of C_1 site symmetry. The main characteristic of the structure is that it contains $[VO_4]$ (Td) tetrahedra and complex B_6O_{13} groups with three boron-oxygen rings. Furthermore, one of the rings is formed by one BO_3 (D_{3h}) triangle and two BO_4 (Td) tetrahedra. The full vibrational representation Γ according to the irreducible representations of C_{2v} for $Na_3VO_2B_6O_{11}$ contains $69A_1+69A_2+69B_1+69B_2$ modes. $A_1+B_1+B_2$ are acoustical modes and $68A_1+69A_2+68B_1+68B_2$ are optical modes. All of these modes are Raman active.

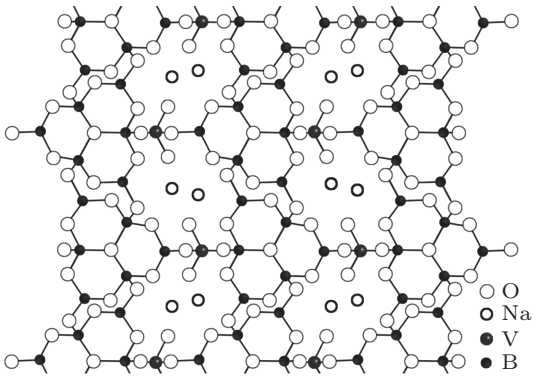


Fig. 1. Projection of structure of $Na_3VO_2B_6O_{11}$ crystal in the (001) plane.

3.2. Raman spectrum at room temperature

The Raman spectrum at room temperature (300 K) is illustrated in Fig. 2. The assignment of the internal vibrational modes in NVBO is rendered difficult by the structure complexity. A significant contribution to the Raman spectra of NVBO comes from the vibration of a low-symmetric polyborate B_6O_{13} group consisting of three boroxygen rings and each ring contains one BO_3 triangle and two BO_4 tetrahedra. However, these groups are not independent of each other in the crystal, so the vibrational modes will be assigned according to the vibration modes of BO_3 and BO_4 groups in their free ion state and some similarities with other borate compounds such as $Li_2B_4O_7$, $CsLiB_6O_{10}$, and LiB_3O_5 crystals.

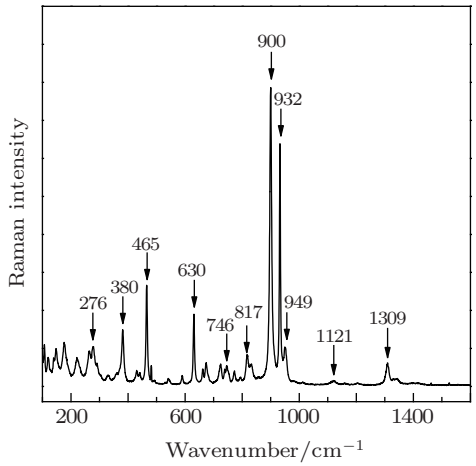


Fig. 2. Raman spectrum of $Na_3VO_2B_6O_{11}$ crystal at room temperature.

A planar equilateral triangle molecule BO_3 with D_{3h} symmetry in its free ion state has four normal vibrational modes. These normal modes are non-degenerate symmetric B–O stretching vibration (ν_s), non-degenerate out-of-plane B–O bending vibration (δ), doubly degenerate B–O stretching vibration (ν_{as}) and doubly degenerate in-plane O–B–O bending vibration (γ). It is known that the normal mode frequencies of the BO_3 group in the vibrational spectra of the bismuth borate crystals are typically situated as follows:[14] $\nu_s \sim 900$–1000 cm^{-1}, $\delta \sim 650$–800 cm^{-1}, $\nu_{as} \sim 1250$–1450 cm^{-1}, and $\gamma \sim 590$–680 cm^{-1}. Elbelrhiti *et al.*[15] reported the Raman spectra of $Li_2B_4O_7$ crystal which contains a basic building block of two BO_4 tetrahedra linked by a common oxygen atom, forming a B_2O_7 group joining two planar triangles BO_3 using the common oxygen atoms. The Raman peaks at 976 cm^{-1} and 968 cm^{-1} are observed and assigned to symmetric stretch vibration of BO_3 in the spectra of $Li_2B_4O_7$ crystal. The 762 cm^{-1} and 739 cm^{-1} peaks are related to the BO_3 symmetric deformation, 1447 cm^{-1} peaks to BO_3 asymmetric stretch. These arguments make the following tentative assignments possible: the strong Raman peak located at 1309 cm^{-1} is due to ν_{as} vibration of B–O bonds in BO_3 groups; the strong peak located at 932 cm^{-1} is related to the ν_s mode; and the peak at 773 cm^{-1} due to the non-degenerate B–O bending vibration mode (δ). Finally, the Raman peak located at 630 cm^{-1} is assigned to the O–B–O bending vibration (γ) in BO_3 triangles, as listed in Table 1.

Table 1. Raman shift and assignment for the $Na_3VO_2B_6O_{11}$ crystal at room temperature.

Wavenumber/cm^{-1}	Assignment	References
380	O–V–O bending in [VO_4]	[25]
465	B–O symmetric stretching in [BO_4]	[24]
630	O–B–O bending in [BO_3]	[14]
746	ring-breathing in [B_3O_6]	[18]–[22]
773	non-degenerate B–O bending in [BO_3]	[15]
817	V–O asymmetric stretching in [VO_4]	[25] and [26]
900	V–O symmetric stretching in [VO_4]	[25]
932	B–O symmetric stretching in [BO_3]	[15]
1119	asymmetric stretching in [BO_4]	[24]
1309	B–O asymmetric stretching in [BO_3]	[14] and [15]

In addition, the BO_3 triangles are connected with BO_4 tetrahedra by B–Ø–B bonds (Ø = bridge oxygen) to form boroxol rings. Such a group with six-numbered B–O rings has been described in several borates. According to Refs. [16] and [17], the nonplanar boroxygen ring can be equivalent to a planar six-membered ring B_3O_6, and the vibrational bands of the crystal with this kind of ring can be attributed to the vibrational modes of the B_3O_6 ring and BO_4 tetrahedra. It is well known that 805 cm^{-1} band, characteristic of vitreous B_2O_3, is assigned to the symmetric breathing vibration of the six-numbered ring[18] which involves the motion of ring oxygen atoms only.[19] Meanwhile the phenomenon of frequency shift toward low wavenumber with the increase of the number of BO_4 tetrahedron in the rings has also been observed recently in studies on boron-oxygen glasses.[20] The structure of $CsLiB_6O_{10}$ (CLBO) crystal, reported by Wang,[17] comprises the basic structure unit (B_3O_7) group which is a six-numbered ring in which two of the B atoms are three-fold coordinated and the third B atom is four-fold coordinated by O atoms. The Raman bands in the range of 782–785 cm^{-1} observed in the spectra of CLBO crystal are assigned the ring-breathing vibrational mode of the six-numbered ring. The frequency of this mode shifts to 765 cm^{-1} observed in the Raman spectrum of LiB_3O_5 (LBO) crystal[21,22] consisting of boroxygen rings with one BO_4 tetrahedron. Therefore, the vibrational band at 746 cm^{-1} in the Raman spectra of NVBO crystal may be related to the breathing vibration of the boroxygen ring which consists of two BO_4 tetrahedra. It is worth noting that its frequency of Raman vibration is lower than those of LBO and CLBO crystals with the same triborate group. On the other hand, the two BO_4 tetrahedra connect together with B–O–B bonds in the boroxygen ring. A tetrahedron molecule BO_4 with symmetry Td has four normal vibrational modes: v_1 (symmetric stretching mode), v_2 (bending mode), v_3 (asymmetric stretching mode), and v_4 (bending mode). The normal mode frequencies for a BO_4 tetrahedron may be approximated by Murray and Lockwood:[23] $v_1 \sim 400$ cm^{-1}, $v_2 \sim 200$ cm^{-1}, $v_3 \sim 1100$ cm^{-1}, and $v_4 \sim 260$ cm^{-1}. Here, the weak band located at 1119 cm^{-1} (A_1 mode) is related to BO_4 asymmetric stretching mode vibration which is observed in the range of 1143–1166 cm^{-1} in the spectra of $LiNaB_4O_7$ as reported by Maczka;[24] the middle intense band at 465 cm^{-1} is caused by the symmetric stretching mode vibration.

In the structure of the NVBO crystal, a three-dimensional framework is formed by VO_4 tetrahedra which, with V–O–B bonds, link sheets made up of polyborate [B_6O_{13}] groups. The VO_4 tetrahedra have four normal vibrational modes. Ross[25] reported the infrared and Raman spectra of the free VO_4 ion. There are four vibrations for VO_4, namely, the v_1 (A_1) symmetric stretching mode located at around 874 cm^{-1}, the v_2 (E) bending mode in the region between 340 cm^{-1} and 345 cm^{-1}, the v_3 (F_2) asymmetric stretching mode at 855 cm^{-1} and the v_4 (F_2) bending mode at 345 cm^{-1}. Ross also reported the v_3 modes of vanadinites at 800 cm^{-1} and 736 cm^{-1} and the v_4 modes around 419 cm^{-1}, 380 cm^{-1} and 322 cm^{-1}. Moreover, according to the analysis of the spectra of Pb5(VO4)Cl, Ray *et al.*[26] reported that the Raman bands located at 879 cm^{-1} and 827 cm^{-1} are assigned to the v_1 symmetric stretching vibration of the VO_4 ion and the Raman bands at 815 and 790 cm^{-1} to the v_3 mode. In this work we assigned the intense band 900 cm^{-1} as relative to the v_1 symmetric stretching vibration. The band located at 817 cm^{-1} is related to the v_3 mode. In addition, the middle intense band located at 380 cm^{-1} is due to O–V–O bending vibration mode. This assignment is in agreement with that proposed by Ray (v_4 in the range of 380–395 cm^{-1}).

3.3. High-temperature Raman spectra

The temperature-dependent Raman spectra of an NVBO crystal in the wavenumber range of 100–1600 cm^{-1} were recorded with temperature increasing from room temperature to melting point, as shown in Fig. 3. Nearly all the vibrational modes exhibit a decrease in wavenumber. Figures 4 and 5 illustrate the wavenumber shifts of main Raman peaks. The Raman bands, such as 630 cm^{-1}, 744 cm^{-1}, 900 cm^{-1}, and 930 cm^{-1}, have wavenumber shifts more than 6 cm^{-1}. In particular, the Raman band located at 1309 cm^{-1} has 22 cm^{-1} wavenumber shifts. According to the report of Cerderira,[27] the decrease in wavenumber with the increase of temperature is ascribed to the increase in the inter-atomic distance in the NVBO crystal when the crystal is heated. In addition, the Raman bands become wider during the heating process. The intense band at 900 cm^{-1} becomes a shoulder at 930 cm^{-1} after the temperature increases to 375 °C, as a consequence of larger distributions of the bonding angles and distances at higher temperature. These phenomena also appear in the high-temperature Raman spectra of $Bi_{12}SiO_{20}$, $KTa1_{1-x}Nb_xO_3$, $Ba_3(PO_4)_2$, BiB_3O_6, and $Bi_2ZnOB_2O_6$ crystals.[28–32] The weak band at 950 cm^{-1} becomes overlapped and merges together with the band at 930 cm^{-1} after the temperature increases to 150 °C. However, the spectra of the NVBO crystal

do not show any splitting or new bands, which indicates that no phase transition occurs under 525 °C in the present study.

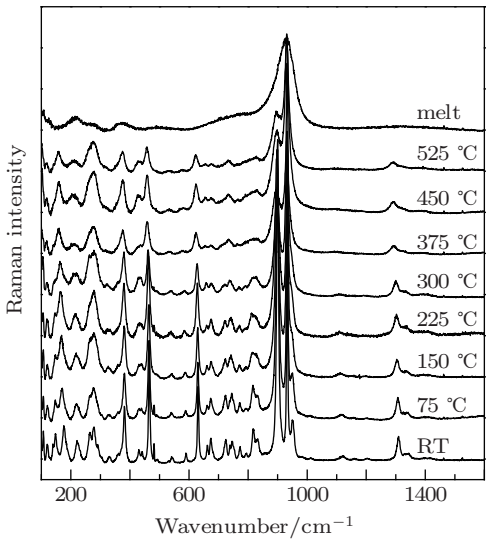


Fig. 3. High-temperature Raman spectra of $Na_3VO_2B_6O_{11}$ crystal from room temperature to melting point.

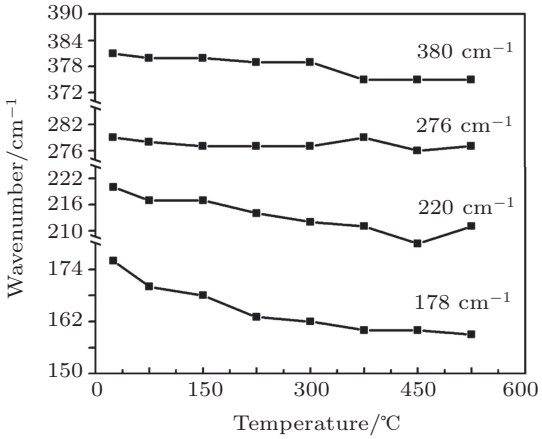


Fig. 4. The wavenumber shifts of Raman peaks with temperature increasing at different frequencies. The lines from top to bottom mean 380 cm^{-1}, 276 cm^{-1}, 220 cm^{-1}, and 178 cm^{-1}, respectively.

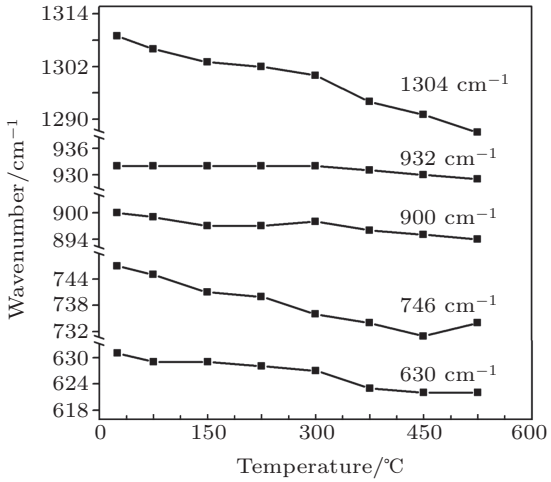


Fig. 5. The wavenumber shifts of Raman peaks with temperature increasing at different frequencies. The lines from top to bottom mean 1304 cm^{-1}, 932 cm^{-1}, 900 cm^{-1}, 746 cm^{-1} and 630 cm^{-1}, respectively.

However, the Raman spectrum of NVBO crystal becomes dramatic when the temperature increases to the melting point (about 610 °C). Some Raman bands, such as 176, 278, 465 and 630 cm^{-1}, disappeared in the spectrum of the melt due to the transformation of the crystal structure during melting. It should be noted that vanishing of the band at 465 cm^{-1} related to the BO_4 vibration implies the break of B–Ø bonds in BO_4 tetrahedron and change from the 4- to 3-coordinated boron during melting.

3.4. Raman spectra of the melt

The fitting results in the range of 600–1100 cm^{-1} are shown in Fig. 6 to explain the micro-structure of the melt. It is reported by some authors that atom clusters exist in the melt. In order to investigate the atom clusters in the melt, the *ab initio* calculation was performed with Gaussian98W program.[33] The Raman spectra of two model clusters, VO_4 tetrahedron and VBO_6 cluster made up of VO_4 tetrahedron and BO_3 triangle connected by one bridge oxygen, are calculated by a restricted Hatree–Fock method of the quantum chemistry *ab initio* calculation[34] with the 6–31G(d) basis set. Experimental spectra have also been presented to make a comparison with the calculated results. The main vibrational bands between the curve calculated and fitting results agree approximately well with each other as a whole. The Raman bands can be recognized with the aid of the GaussView software. The vibration bands at 928 cm^{-1} (934 cm^{-1} in calculation) and 1300 cm^{-1} (1294 cm^{-1} in calculation) are related to the B–O stretching vibrations in VBO_6 clusters. The band located at 797 cm^{-1} (786 cm^{-1} in calculation) can be assigned as the bending vibration of B–Ø–V bridge oxygen. It also demonstrated that the bands at 884 cm^{-1} (893 cm^{-1} in calculation) and 946 cm^{-1} (944 cm^{-1} in calculation) represent the V–O vibration of free

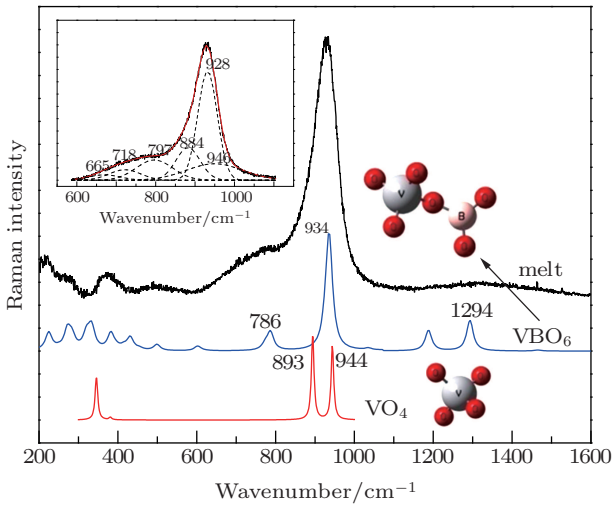


Fig. 6. (color online) Raman spectra of melt of $Na_3VO_2B_6O_{11}$ crystal and calculation of VO_4 and VBO_6 groups; the fitting result in the shoulder picture.

VO_4 tetrahedron. These arguments make the following conclusion that the crystal framework collapses with the break of B–Ø bonds in BO_4 tetrahetra to form VO_4 and VBO_6 clusters existing in the melt.

4. Conclusion

High-temperature Raman spectroscopy has been used to investigate the micro-structure of NVBO crystals and its melt. The obtained results coincided well with experimental results. Raman spectra of single crystal NVBO were recorded in the spectral range of 10–1600 cm^{-1} at room temperature first. Then 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 temperature increasing. No phase transition was observed under 525 °C. Lastly, the micro-structure of its melt was studied by quantum chemistry *ab initio* method. The VO_4 and VBO_6 clusters exist in the melt.

Acknowlegments

The authors thank Xinjiang Key Laboratory of Electronic Information Materials, China for providing the NVBO crystal and High Magnetic Field Laboratory of Chinese Academy of Sciences for providing the Raman spectrometer.

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