**Supporting Information.**

Evidence of "new hot spots" from determining the nonlinear optical behavior of materials: mechanism studies on vanadium borate crystal $Na_3VO_2B_6O_{11}$

*Xin Su,* [1, 2] *Zhihua Yang,** [1] *Ming-Hsein Lee,* [3,1] *Shilie Pan,** [1] *Ying Wang,* [1, 2] *Xiaoyun Fan,* [1] *Zhenjun Huang,* [1, 2] *Bingbing Zhang* [1, 2]

[1] Key Laboratory of Functional Materials and Devices for Special Environments of CAS; Xinjiang Key Laboratory of Electronic Information Materials and Devices, Xinjiang Technical Institute of Physics & Chemistry of CAS, 40-1 South Beijing Road, Urumqi 830011, China;

[2] University of Chinese Academy of Sciences, Beijing 100049, China;

[3]Department of Physics, Tamkang University, Taipei 25137, Taiwan

**Corresponding Author**

To whom correspondence should be addressed. Phone: (86)991-3810816

Fax: (86)991-3838957. E-mail: zhyang@ms.xjb.ac.cn (Zhihua Yang).

slpan@ms.xjb.ac.cn (Shilie Pan)

## Experimental Details

**Crystal Growth.** The raw materials were prepared by traditional solid-state reaction following the equation (1), the sample was calcined at 600℃ for two days with several intermediate grindings until a monophasic powder was achieved.

$3Na_2CO_3 + V_2O_5 + 12H_3BO_3 = 2Na_3VO_2B_6O_{11} + 3CO_2\uparrow + 18H_2O\uparrow$.    (1)

Large single crystals of NVB were grown by high temperature flux method using $NaVO_3$ as the flux. We found that high quality single crystals can be grown with NVB: $NaVO_3$ = 1:1 (molar ratio). The mixture was heated to 850℃ and held at this temperature for 24 *h* with continuous stirred to ensure homogeneous of the solution. A high quality seed crystal of NVB (obtained in our previous work) was attached with Pt wire to an alumina rod. The seed test method was employed to measure the saturation point of the solution. Then the seed crystal was introduced into the liquid surface at a few degrees higher than the saturation point for 20 *min* to dissolve the outer surface of the seed crystal. The temperature was lowered quickly to saturation point, and then NVB crystal was grown at a cooling rate of 0.8-1.5℃/day with a seed-rotation rate of 12 *rpm* until the desired size was obtained. Then colorless crystals with dimensions of 30 *mm* × 23 *mm* × 20 *mm* have been obtained in ~15 days as shown inset Fig.2. When the growth of crystal ended, it was lifted out of the liquid surface and cooled to room temperature at a cooling rate of 10℃/*h*.

**Transmittance Spectrum.** Transmittance spectrum was measured by the Perkin-Elmer Lambda 900 *UV-Vis-NIR* spectrophotometer in the wavelength range from 190 to 2600 *nm* at room temperature. A wide transmission range from 410 to 3000 *nm* is observed as shown in Fig.S2. Therefore, NVB is a semiconductor and a potential NLO material due to the wide transparency range. An absorption edge of 370 *nm* and for this reason an optical band gap of about 3.35 eV could be obtained by the extrapolation method.[1]

**Refractive-Index Dispersion Measurements.** The Refractive-Index Dispersion Measurements were performed by the minimum-deviation method between 435 and 694 *nm* at room temperature. Since NVB belongs to $P2_12_12_1$ space group, it is possible to measure $n^x$, $n^y$ and $n^z$ using two prisms. NVB has only one nonzero independent component of the second-order polarizability tensor due to its crystallization in the NCS orthorhombic system, assuming the Kleinman symmetry conditions. The experimental measurements show that NVB is a positive biaxial optical crystal, the dielectric axes *X*, *Y*, *Z* ($n^x > n^y > n^z$) corresponding to crystallographic axes *a*, *b*, *c*, respectively. The refractive indices have been measured by the minimum deviation technique and fitted to the Sellmeier equations. Table S3 shows several typical wavelengths in the visible region measured and fitted refractive index data for $n^x$, $n^y$ and $n^z$. The Sellmeier equations of the crystal have been fitted:

$n_x^2 = 2.57012 + 0.01602085 / (\lambda^2 – 0.05318711) – 0.04219414\lambda^2$, (2)

$n_y^2 = 2.56861 + 0.01966325 / (\lambda^2 – 0.04369535) – 0.06839396\lambda^2$, (3)

$n_z^2 = 2.68801 + 0.01864372 / (\lambda^2 – 0.02062079) – 0.01874858\lambda^2$, (4)

here, $\lambda$ denotes the wavelength in microns. The values calculated from ours are exactly consistent with experimental ones to the forth decimal place.

Single crystals of NVB were grown by high temperature flux method. With bigger size (30 *mm* × 23 *mm* × 20 *mm*) and higher quality insert in Fig.S2 than previously report ones.[2, 3]The transparent areas of NVB range from 410 *nm* to 3000 *nm* as indicated in transmission spectrum Fig.S2 The corresponding absorption edge in the UV side is about 370 *nm* (90%) which can also be revealed from the direct band gap character with the value of 3.28 eV (Table S2). This is in agreement with the previous experimental values[2, 3] of NVB as well as calculated value using the first principles method in this work.

The phase-matching (PM) angles of NVB are calculated based on Sellmeier equations Eqs. (2) - (4)). As shown in Fig. S3 based on the Sellmeier equations, the type I and type II PM curves for SHG are predicted. For NVB, all type I PM with propagation in the three principal planes, but this dispersion cannot be offset which has not possessed a birefringence large enough to meet the type II PM Condition. The SHG of Nd:YAG laser which has wave length 1064 *nm* are possible and the PM angles are $\theta$ = 79.3°, $\varphi$ = 0° and $\theta$ = 47.5°, $\varphi$ = 90° for type I SHG at 1064 *nm* in *ZX* and *YZ* planes, respectively. For type-I PM, the PM ranges of fundamental wavelength are ranging from 427 to 2617 *nm*.

**Figure S1**. The distortion of the $VO_4$ tetrahedron in NVB crystal.

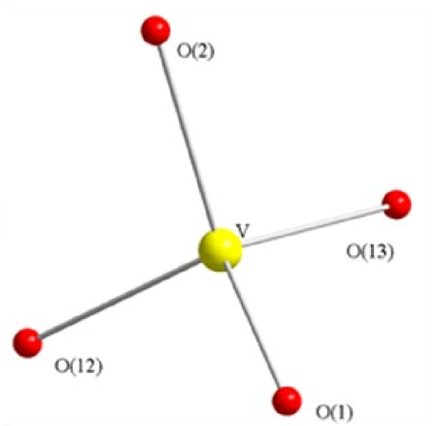


**Figure S2**. Crystal transmission spectrum and crystal photograph.

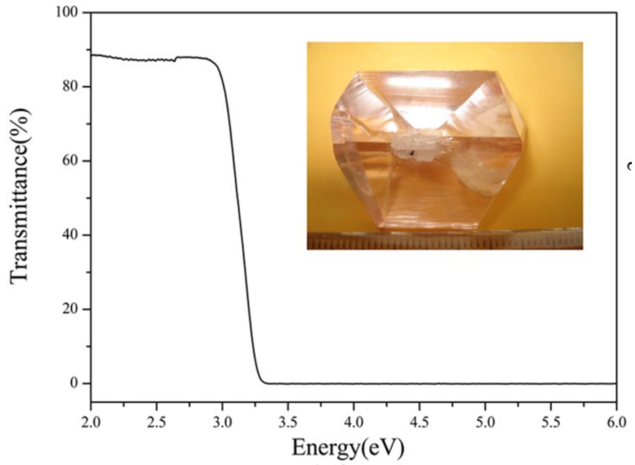


**Figure S3**. The experimental SHG phase matching range.

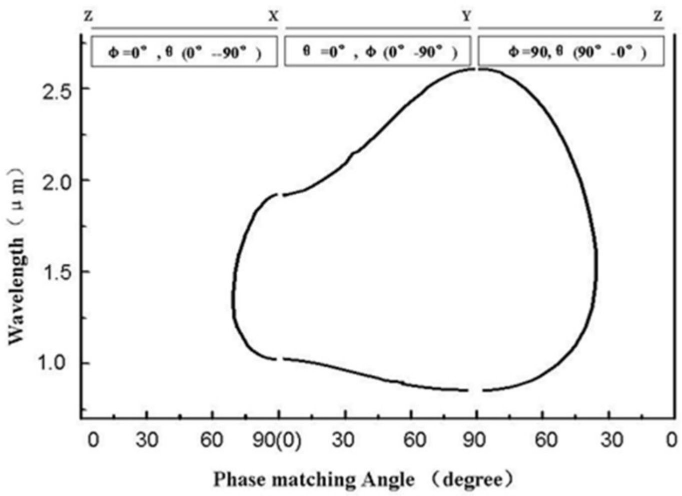


**Table S1**.Selected bond lengths (Å) and angles (deg) for the NVB.

| Parameter | Exp. | Cal. |
|---|---|---|
| V(1)-O(1) | 1.85(5) | 1.84(6) |
| V(1)-O(2) | 1.76(5) | 1.76(9) |
| V(1)-O(12) | 1.64(7) | 1.66(0) |
| V(1)-O(13) | 1.63(7) | 1.66(1) |
| Na(1)-O(4) | 2.37(3) | 2.39(3) |
| Na(1)-O(11) | 2.40(4) | 2.41(5) |
| Na(1-O(10) | 2.51(3) | 2.51(5) |
| Na(1)-O(6) | 2.51(5) | 2.56(1) |
| Na(1)-O(12)#2 | 2.54(1) | 2.47(4) |
| Na(1)-O(13) | 2.65(7) | 2.58(5) |
| Na(1)-O(2)#2 | 2.78(7) | 2.82(7) |
| Na(1)-O(1) | 2.94(8) | 2.93(3) |
| Na(2)-O(1)#4 | 2.34(2) | 2.39(3) |

| | | |
|---|---|---|
| Na(2)-O(7) | 2.58(4) | 2.58(8) |
| Na(2)-O(5) | 2.60(3) | 2.60(8) |
| Na(2)-O(9) | 2.61(1) | 2.58(4) |
| Na(2)-O(10)#5 | 2.66(2) | 2.68(5) |
| Na(2)-O(13) | 2.67(8) | 2.68(3) |
| Na(2)-O(3) | 2.85(2) | 2.84(2) |
| Na(2)-O(11)#4 | 2.87(2) | 2.89(9) |
| Na(3)-O(3)#7 | 2.38(5) | 2.38(7) |
| Na(3)-O(6)#3 | 2.42(5) | 2.43(7) |
| Na(3)-O(12) | 2.43(3) | 2.39(3) |
| Na(3)-O(4)#3 | 2.48(9) | 2.49(4) |
| Na(3)-O(2)#1 | 2.54(6) | 2.51(1) |
| Na(3)-O(7)#8 | 2.56(5) | 2.56(9) |
| Na(3)-O(13)#1 | 2.87(7) | 2.89(4) |
| B(1)-O(7)#9 | 1.46(2) | 1.47(0) |
| B(1)-O(2) | 1.46(4) | 1.47(4) |
| B(1)-O(10)#1 | 1.47(3) | 1.46(6) |
| B(1)-O(8) | 1.52(2) | 1.52(2) |
| B(2)-O(5) | 1.36(3) | 1.36(3) |
| B(2)-O(11)#4 | 1.37(4) | 1.37(4) |
| B(2)-O(7)#8 | 1.37(3) | 1.38(6) |
| B(3)-O(4)#10 | 1.36(3) | 1.36(8) |
| B(3)-O(6) | 1.37(3) | 1.37(4) |
| B(3)-O(1)#10 | 1.37(2) | 1.38(7) |
| B(4)-O(9) | 1.35(3) | 1.36(6) |
| B(4)-O(3) | 1.37(4) | 1.37(6) |
| B(4)-O(10) | 1.38(3) | 1.38(4) |
| B(5)-O(3)#11 | 1.43(7) | 1.44(8) |
| B(5)-O(9) | 1.45(4) | 1.45(2) |
| B(5)-O(4) | 1.47(6) | 1.48(0) |
| B(5)-O(8)#4 | 1.51(3) | 1.52(2) |
| B(6)-O(11) | 1.44(1) | 1.44(2) |
| B(6)-O(5)#10 | 1.44(9) | 1.45(1) |
| B(6)-O(6) | 1.47(4) | 1.47(7) |
| B(6)-O(8)#12 | 1.52(5) | 1.52(8) |
| O(13)-V(1)-O(12) | 106.68(1) | 107.08(5) |
| O(13)-V(1)-O(2) | 109.66(1) | 109.53(0) |
| O(12)-V(1)-O(2) | 109.11(1) | 109.17(7) |
| O(13)-V(1)-O(1) | 104.09(1) | 104.16(1) |
| O(12)-V(1)-O(1) | 106.11(1) | 107.02(6) |
| O(2)-V(1)-O(1) | 120.36(6) | 119.19(5) |
| O(4)-Na(2)-O(11) | 96.42(7) | 94.81(8) |
| O(4)-Na(2)-O(10) | 84.21(6) | 83.34(9) |

| | | |
|---|---|---|
| O(11)-Na(2)-O(10) | 146.32(7) | 143.69(5) |
| O(4)-Na(2)-O(6) | 82.42(7) | 80.05(2) |
| O(11)-Na(2)-O(6) | 56.94(6) | 56.33(7) |
| O(10)-Na(2)-O(6) | 90.02(6) | 89.03(9) |
| O(4)-Na(1)-O(12)#2 | 152.54(7) | 154.35(5) |
| O(11)-Na(1)-O(12)#2 | 81.92(7) | 82.84(6) |
| O(10)-Na(1)-O(12)#2 | 112.24(7) | 112.51(4) |
| O(6)-Na(1)-O(12)#2 | 117.91(7) | 117.33(6) |
| O(4)-Na(1)-O(13) | 82.44(8) | 83.01(7) |
| O(11)-Na(1)-O(13) | 119.06(7) | 121.50(5) |
| O(10)-Na(1)-O(13) | 94.46(7) | 94.45(8) |
| O(6)-Na(1)-O(13) | 163.68(7) | 162.46(4) |
| O(12)#2-Na(1)-O(13) | 74.73(8) | 76.73(0) |
| O(4)-Na(1)-O(2)#2 | 137.61(6) | 136.85(6) |
| O(11)-Na(1)-O(2)#2 | 118.15(6) | 117.53(3) |
| O(10)-Na(1)-O(2)#2 | 53.40(5) | 52.95(4) |
| O(6)-Na(1)-O(2)#2 | 95.93(6) | 94.25(2) |
| O(12)#2-Na(1)-O(2)#2 | 62.72(5) | 62.27(9) |
| O(13)-Na(1)-O(2)#2 | 99.35(6) | 99.24(4) |
| O(4)-Na(1)-O(1) | 51.55(5) | 51.96(9) |
| O(11)-Na(1)-O(1) | 73.46(5) | 73.28(6) |
| O(10)-Na(1)-O(1) | 128.20(5) | 128.12(0) |
| O(6)-Na(1)-O(1) | 106.59(6) | 105.93(8) |
| O(12)#2-Na(1)-O(1) | 102.52(6) | 81.78(5) |
| O(13)-Na(1)-O(1) | 58.67(5) | 57.79(8) |
| O(2)#2-Na(1)-O(1) | 157.24(6) | 155.99(5 |
| O(1)#4-Na(2)-O(7) | 97.63(6) | 96.26(9) |
| O(1)#4-Na(2)-O(5) | 83.85(6) | 82.50(0) |
| | Exp. | Cal. |
| O(7)-Na(2)-O(5) | 113.46(7) | 112.41(1) |
| O(1)#4-Na(2)-O(9) | 83.32(6) | 82.500(0) |
| O(7)-Na(2)-O(9) | 169.35(7) | 170.38(6) |
| O(5)-Na(2)-O(9) | 77.19(5) | 76.96(7) |
| O(1)#4-Na(2)-O(10)#5 | 96.43(6) | 95.21(0) |
| O(7)-Na(2)-O(10)#5 | 54.46(4) | 54.29(3) |
| O(5)-Na(2)-O(10)#5 | 167.89(7) | 166.40(2) |
| O(9)-Na(2)-O(10)#5 | 114.90(6) | 116.22(0) |
| O(1)#4-Na(2)-O(13) | 156.38(8) | 156.99(0) |
| O(7)-Na(2)-O(13) | 94.35(6) | 95.81(6) |
| O(5)-Na(2)-O(13) | 109.83(7) | 110.30(9) |
| O(9)-Na(2)-O(13) | 81.26(7) | 82.32(2) |
| O(10)#5-Na(2)-O(13) | 74.26(7) | 76.26(4) |
| O(1)#4-Na(2)-O(3) | 75.79(6) | 74.67(1) |

| | | |
|---|---|---|
| O(7)-Na(2)-O(3) | 120.14(6) | 120.34(7) |
| O(5)-Na(2)-O(3) | 124.38(6) | 124.08(0) |
| O(9)-Na(2)-O(3) | 49.71(6) | 50.10(2) |
| O(10)#5-Na(2)-O(3) | 67.09(6) | 67.75(2) |
| O(13)-Na(2)-O(3) | 80.59(6) | 82.32(7) |
| O(1)#4-Na(2)-O(11)#4 | 75.79(6) | 74.01(8) |
| O(7)-Na(2)-O(11)#4 | 66.35(6) | 65.60(0) |
| O(5)-Na(2)-O(11)#4 | 49.54(5) | 49.18(8) |
| O(9)-Na(2)-O(11)#4 | 123.91(6) | 122.73(7) |
| O(10)#5-Na(2)-O(11)#4 | 118.73(6) | 117.31(6) |
| O(13)-Na(2)-O(11)#4 | 127.78(7) | 121.39(5) |
| O(3)-Na(2)-O(11)#4 | 151.49(5) | 148.61(5) |
| O(3)#7-Na(3)-O(6)#3 | 94.83(7) | 93.28(6) |
| O(3)#7-Na(3)-O(12) | 111.74(8) | 111.34(3) |
| O(6)#3-Na(3)-O(12) | 89.84(8) | 91.02(3) |
| O(3)#7-Na(3)-O(4)#3 | 57.69(6) | 57.69(2) |
| O(6)#3-Na(3)-O(4)#3 | 81.95(7) | 80.18(8) |
| O(12)-Na(3)-O(4)#3 | 165.64(7) | 154.48(3) |
| O(3)#7-Na(3)-O(2)#1 | 122.28(6) | 123.37(9) |
| O(6)#3-Na(3)-O(2)#1 | 138.74(7) | 138.87(8) |
| O(12)-Na(3)-O(2)#1 | 91.99(7) | 91.97(5) |
| O(4)#3-Na(3)-O(2)#1 | 101.96(6) | 102.78(2) |
| O(3)#7-Na(3)-O(7)#8 | 149.26(7) | 148.12(0) |
| O(6)#3-Na(3)-O(7)#8 | 83.89(6) | 83.61(6) |
| O(12)-Na(3)-O(7)#8 | 98.98(7) | 100.45(2) |
| O(4)#3-Na(3)-O(7)#8 | 91.87(6) | 90.61(8) |
| O(2)#1-Na(3)-O(7)#8 | 55.12(5) | 55.75(8) |
| O(12)-Na(3)-O(13)#1 | 72.38(9) | 72.32(7) |
| O(4)#3-Na(3)-O(13)#1 | 111.33(7) | 111.74(6) |
| O(2)#1-Na(3)-O(13)#1 | 61.37(5) | 62.00(0) |
| O(7)#8-Na(3)-O(13)#1 | 115.52(7) | 117.00(6) |
| O(7)#9-B(1)-O(2) | 107.88(1) | 107.62(0) |
| O(7)#9-B(1)-O(10)#1 | 109.86(1) | 109.10(5) |
| O(2)-B(1)-O(10)#1 | 109.21(1) | 109.10(5) |
| O(7)#9-B(1)-O(8) | 109.11(1) | 108.79(1) |
| O(2)-B(1)-O(8) | 111.88(1) | 111.79(6) |
| O(10)#1-B(1)-O(8) | 108.88(1) | 109.52(1) |
| O(5)-B(2)-O(11)#4 | 114.9(2) | 115.09(7) |
| O(5)-B(2)-O(7)#8 | 123.4(3) | 122.99(8) |
| O(11)#4-B(2)-O(7)#8 | 121.6(2) | 121.77(7) |
| O(4)#10-B(3)-O(6) | 120.50(1) | 120.98(0) |
| O(4)#10-B(3)-O(1)#10 | 119.6(2) | 119.70(3) |

| | | |
|---|---|---|
| O(6)-B(3)-O(1)#10 | 119.9(2) | 119.29(1) |
| O(9)-B(4)-O(3) | 115.4(2) | 115.56(2) |
| O(9)-B(4)-O(10) | 123.0(3) | 122.65(3) |
| O(3)-B(4)-O(10) | 121.4(2) | 121.61(9) |
| O(3)#11-B(5)-O(9) | 113.91(1) | 114.05(7) |
| O(3)#11-B(5)-O(4) | 107.75(1) | 107.67(8) |
| O(9)-B(5)-O(4) | 109.8(2) | 109.99(5) |
| O(3)#11-B(5)-O(8)#4 | 108.67(1) | 108.65(3) |
| O(9)-B(5)-O(8)#4 | 107.41(1) | 106.95(4) |
| O(4)-B(5)-O(8)#4 | 109.28(1) | 109.33(5) |
| O(11)-B(6)-O(5)#10 | 114.21(1) | 114.51(9) |
| O(11)-B(6)-O(6) | 107.28(1) | 107.39(2) |
| O(5)#10-B(6)-O(6) | 109.8(2) | 109.30(9) |
| O(11)-B(6)-O(8)#12 | 108.66(1) | 108.65(3) |
| O(5)#10-B(6)-O(8)#12 | 107.37(1) | 106.94(5) |
| O(6)-B(6)-O(8)#12 | 109.46(1) | 109.30(9) |
| O(12)-Na(3)-O(13)#1 | 72.38(9) | 72.32(7) |
| O(4)#3-Na(3)-O(13)#1 | 111.33(7) | 111.74(6) |
| O(2)#1-Na(3)-O(13)#1 | 61.37(5) | 62.00(4) |
| O(7)#8-Na(3)-O(13)#1 | 115.52(7) | 117.00(6) |
| O(7)#9-B(1)-O(2) | 107.88(1) | 107.62(0) |
| O(7)#9-B(1)-O(10)#1 | 109.86(1) | 110.00(1) |
| O(2)-B(1)-O(10)#1 | 109.21(1) | 109.10(5) |
| O(7)#9-B(1)-O(8) | 109.11(1) | 108.79(1) |
| O(2)-B(1)-O(8) | 111.88(1) | 111.77(6) |
| O(10)#1-B(1)-O(8) | 108.88(1) | 109.52(1) |
| O(5)-B(2)-O(11)#4 | 114.92 (0) | 115.09(7) |
| O(5)-B(2)-O(7)#8 | 123.43 (0) | 122.99(8) |

Symmetry transformations used to generate equivalent atoms:

#1 -x+1, y+1/2, -z+1/2 #2 -x+1, y-1/2, -z+1/2
#3 -x+2, y+1/2, -z+1/2 #4 -x+3/2, -y+2, z-1/2
#5 x-1/2, -y+3/2, -z #6 -x+1/2, -y+2, z-1/2
#7 -x+3/2, -y+2, z+1/2 #8 x+1/2, -y+5/2, -z
#9 -x+1/2, -y+2, z+1/2 #10 -x+2, y-1/2, -z+1/2
#11 x+1/2, -y+3/2, -z #12 x+1/2, -y+3/2, -z+1

**Table S2**. State energies (eV) of the highest valence band (H-VB) and the lowest conduction band (L-CB) at same k-points of NVB.

| compound | K-piont | H-VB (eV) | L-CB (eV) |
|---|---|---|---|
| $Na_3VO_2B_6O_{11}$ | G (0.000, 0.000, 0.000) | 0 | 3.27882 |
| | Z (0.000, 0.000, 0.500) | -0.10979 | 3.36635 |
| | T (-0.500,0.000, 0.000) | -0.28818 | 3.37276 |
| | Y(-0.500,0.000, 0.000) | -0.48827 | 3.37265 |
| | S (-0.500,0.500, 0.000) | -0.53342 | 3.43772 |
| | X (0.000,0.500, 0.000) | -0.71182 | 3.42918 |
| | U (0.000, 0.500, 0.500) | -0.78501 | 3.42303 |
| | R (0.500, 0.500, 0.500) | -0.86621 | 3.42705 |

**Table S3**. The experimental values of refractive indices were measured several wavelengths at room temperature.

| Wavelength | $n^x$ | $n^y$ | $n^z$ | $n^z$-$n^x$ |
|---|---|---|---|---|
| 0.4047 | 1.6465 | 1.6571 | 1.6923 | 0.0458 |
| 0.4078 | 1.6454 | 1.6561 | 1.6909 | 0.0455 |
| 0.4200 | 1.6416 | 1.6524 | 1.6859 | 0.0442 |
| 0.4358 | 1.6374 | 1.6483 | 1.6804 | 0.0430 |
| 0.4500 | 1.6341 | 1.6450 | 1.6762 | 0.0420 |
| 0.4860 | 1.6275 | 1.6383 | 1.6679 | 0.0404 |
| 0.4880 | 1.6272 | 1.6380 | 1.6675 | 0.0403 |
| 0.4916 | 1.6267 | 1.6374 | 1.6669 | 0.0402 |
| 0.4962 | 1.6260 | 1.6367 | 1.6660 | 0.0401 |
| 0.5145 | 1.6235 | 1.6342 | 1.6630 | 0.0396 |
| 0.5320 | 1.6214 | 1.6320 | 1.6605 | 0.0392 |
| 0.5461 | 1.6198 | 1.6304 | 1.6587 | 0.0389 |

| | | | | |
|---|---|---|---|---|
| 0.5688 | 1.6176 | 1.6281 | 1.6562 | 0.0386 |
| 0.5770 | 1.6168 | 1.6274 | 1.6554 | 0.0385 |
| 0.5790 | 1.6167 | 1.6272 | 1.6552 | 0.0385 |
| 0.5893 | 1.6158 | 1.6263 | 1.6542 | 0.0384 |
| 0.6123 | 1.6140 | 1.6245 | 1.6522 | 0.0382 |
| 0.6234 | 1.6132 | 1.6237 | 1.6513 | 0.0381 |
| 0.6328 | 1.6125 | 1.6231 | 1.6506 | 0.0381 |
| 0.6561 | 1.6110 | 1.6216 | 1.6490 | 0.0380 |
| 0.6907 | 1.6090 | 1.6196 | 1.6469 | 0.0379 |
| 0.6943 | 1.6088 | 1.6194 | 1.6467 | 0.0379 |
| 0.8000 | 1.6036 | 1.6148 | 1.6417 | 0.0381 |
| 0.9000 | 1.5996 | 1.6116 | 1.6382 | 0.0386 |
| 1.0140 | 1.5954 | 1.6085 | 1.6348 | 0.0394 |
| 1.0640 | 1.5936 | 1.6073 | 1.6334 | 0.0399 |
| 1.3200 | 1.5842 | 1.6017 | 1.6268 | 0.0427 |
| 1.5500 | 1.5749 | 1.5968 | 1.6208 | 0.0459 |

The data were fitted using Sellmeier equations (see in text Eqs. (2) - (4)) in Table S3.

**Table** S4. The nonzero elements of $\chi^{(2)}$ expected for NVB crystal in point group *222*.

| $Na_3VO_2B_6O_{11}$ | | | | |
|---|---|---|---|---|
| Plane | $n^z > n^y > n^x$ | | $n^z < n^y < n^x$ | |
| XY | $d_{14}\sin 2\varphi$ | type II$^{(-)}$ | $-d_{14}\sin 2\varphi$ | type I$^{(+)}$ |
| YZ | $d_{14}\sin 2\theta$ | type I$^{(+)}$ | $d_{14}\sin 2\theta$ | type II$^{(-)}$ |
| XZ $\theta < V_Z$ | $-d_{14}\sin 2\theta$ | type II$^{(-)}$ | $-d_{14}\sin 2\theta$ | type I$^{(+)}$ |

| | | | | |
|---|---|---|---|---|
| θ > $V_Z$ | $-d_{14}$ sin2θ | type I$^{(+)}$ | $-d_{14}$ sin2θ | type II$^{(-)}$ |

References


(1) Schevciw, O.; White, W. B. *Mater. Res. Bull.* **1983**, *18*, 1059-1068.

(2) Fan, X.Y.; Pan, S. L.; Han, J.; Tian, X. L.; Zhou, Z. X., *J. Syn. Cryst.***2010**, *39*, 35-42.

(3) Fan, X.Y.; Pan, S. L.; Hou, X. L.; Tian, X. L.; Han, *J. Cryst. Growth Des*. **2010**, *10*, 252- 256; *J. Cryst .Growth* **2010**, *312*, 2263-2266.