# Cd$_4$InO(BO$_3$)$_3$: A New Nonlinear Optical Crystal Exhibiting Strong Second Harmonic Generation Effect and Moderate Birefringence

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# *Content*

**Table S1.** Crystal data and structure refinement for $Cd_4InO(BO_3)_3$.

| | |
|---|---|
| Chemical formula | $Cd_4InO(BO_3)_3$ |
| Formula weight | 756.85 g/mol |
| Temperature | 298(2) K |
| Wavelength | 0.71073 Å |
| Crystal system | monoclinic |
| Space group | *Cm* |
| Unit cell dimensions ( Å) | a = 7.880(2) |
| | b = 15.729(4) |
| | c = 3.3994(8) |
| $\beta$ (°) | 99.871 (10) |
| Volume, Z | 415.10(18) Å$^3$, 2 |
| Density (calculated) | 6.055 g/cm$^3$ |
| Theta range for data collection | 2.59 to 24.91° |
| Index ranges | -9<=h<=9, -18<=k<=18, -4<=l<=3 |
| Coverage of independent reflections | 99 % |
| Reflections collected | 1986 |
| Independent reflections ($R_{int}$) | 0.0374 |
| Refinement method | Full-matrix least-squares on F$^2$ |
| Goodness-of-fit on F$^2$ | 1.043 |
| Final R indices I>2σ(I) | $R_1$=0.0200, w$R_2$=0.0462 |
| all data | $R_1$=0.0201, w$R_2$=0.0462 |
| Largest diff. peak and hole | 0.667 and -0.639 eÅ$^{-3}$ |

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $wR_2 = [\Sigma w(F_o^2 – F_c^2)^2 / \Sigma w\ F_o^4]^{1/2}$ for $F_o^2 > 2\sigma(\ F_o^2)$.

**Table S2.** Atomic coordinates and equivalent isotropic atomic displacement parameters ($\text{Å}^2$) for $Cd_4InO(BO_3)_3$.

| Atoms | x/a | y/b | z/c | U(eq) | BVS |
|---|---|---|---|---|---|
| In1 | 0.86175(15) | 0.5 | 0.1551(3) | 0.0127(3) | 3.031 |
| Cd1 | 0.50451(11) | 0.38768(5) | 0.48776(19) | 0.0121(3) | 2.230 |
| Cd2 | 0.11470(13) | 0.32300(6) | 0.7890(2) | 0.0183(3) | 1.917 |
| O1 | 0.0602(18) | 0.5 | 0.752(4) | 0.021(3) | 2.003 |
| O2 | 0.6779(17) | 0.5 | 0.575(4) | 0.017(3) | 1.871 |
| O3 | 0.3273(13) | 0.2721(6) | 0.437(3) | 0.025(2) | 1.922 |
| O4 | 0.3221(11) | 0.4242(5) | 0.919(3) | 0.0168(19) | 2.145 |
| O5 | 0.6364(13) | 0.3205(5) | 0.034(3) | 0.0180(19) | 2.041 |
| O6 | 0.9353(11) | 0.3595(5) | 0.223(3) | 0.0148(18) | 2.045 |
| B1 | 0.234(3) | 0.5 | 0.867(6) | 0.012(4) | 2.920 |
| B2 | 0.8027(18) | 0.3012(9) | 0.226(4) | 0.012(3) | 3.124 |

Symmetry transformations used to generate equivalent atoms:
#1 x,y,z+1 #2 x,y,z-1 #3 x-1/2,y-1/2,z #4 x-1/2,y-1/2,z+1 #5 x+1/2,-y+1/2,z #6 x+1/2,-y+1/2,z+1 #7 x+1/2,y+1/2,z-1 #8 x+1/2,y+1/2,z #9 x,-y+1,z #10 x-1/2,y+1/2,z #11 x-1/2,-y+1/2,z #12 x-1/2,-y+1/2,z-1 #13 x+1/2,y-1/2,z.

**Table S3.** Bond lengths (Å) for $Cd_4InO(BO_3)_3$.

| bonds | lengths | bonds | lengths |
|-------|---------|-------|---------|
| In1-O5 | 2.110(2) | In1-O5 | 2.110(3) |
| In1-O1 | 2.140(2) | In1-O3 | 2.226(14) |
| In1-O3 | 2.226(14) | In1-O1 | 2.140(2) |
| Cd1-O5 | 2.200(15) | Cd1-O6 | 2.208(15) |
| Cd1-O2 | 2.265(13) | Cd1-O4 | 2.279(14) |
| Cd1-O6 | 2.280(14) | Cd1-O4 | 2.296(13) |
| Cd2-O3 | 2.238(14) | Cd2-O3 | 2.294(13) |
| Cd2-O4 | 2.294(14) | Cd2-O2 | 2.366(14) |
| Cd2-O6 | 2.431(14) | Cd2-O2 | 2.366(14) |
| Cd2-O2 | 2.366(14) | Cd2-O3 | 2.801(3) |
| O2-B1 | 1.440(3) | O1-B2 | 1.390(4) |
| O4-B2 | 1.340(2) | O3-B1 | 1.340(3) |
| O4-B2 | 1.340(2) | O6-B1 | 1.370(3) |

**Table S4.** Bond angles (°) for $Cd_4InO(BO_3)_3$.

| bonds | angles | bonds | angles |
|---|---|---|---|
| O5-In1-O1 | 81.2(8) | O5-In1-O1 | 178.7(8) |
| O1-In1-O1 | 94.9(7) | O3-In1-O1 | 77.6(4) |
| O3-In1-O1 | 77.6(4) | O5-Cd1-O6 | 94.6(7) |
| O5-Cd1-O2 | 176.2(8) | O6-Cd1-O2 | 83.4(6) |
| O5-Cd1-O4 | 100.5(7) | O6-Cd1-O4 | 164.8(5) |
| O2-Cd1-O4 | 81.4(6) | O5-Cd1-O6 | 97.5(7) |
| O6-Cd1-O6 | 98.2(6) | O2-Cd1-O6 | 86.0(5) |
| O4-Cd1-O6 | 80.5(5) | O5-Cd1-O4 | 97.4(7) |
| O6-Cd1-O4 | 81.7(5) | O2-Cd1-O4 | 79.1(5) |
| O4-Cd1-O4 | 95.7(5) | O6-Cd1-O4 | 165.0(5) |
| O3-Cd2-O4 | 109.0(5) | O3-Cd2-O3 | 96.9(5) |
| O3-Cd2-O2 | 92.3(5) | O3-Cd2-O4 | 103.5(5) |
| O4-Cd2-O2 | 77.0(5) | O3-Cd2-O2 | 170.0(5) |
| O3-Cd2-O6 | 91.2(5) | O3-Cd2-O6 | 119.8(5) |
| O2-Cd2-O6 | 80.7(5) | O4-Cd2-O6 | 126.7(5) |
| O3-Cd2-O2 | 84.9(5) | O3-Cd2-O2 | 176.0(5) |
| O2-Cd2-O2 | 85.7(5) | O4-Cd2-O2 | 73.9(5) |
| O3-B1-O6 | 123.6(19) | O6-Cd2-O2 | 56.5(5) |
| O6-B1-O2 | 117.1(17) | O3-B1-O2 | 119.3(19) |
| O4-B2-O4 | 119.(3) | O4-B2-O1 | 120.5(15) |
| O4-B2-O1 | 120.5(15) | O5-In1-O1 | 178.7(8) |
| O5-In1-O1 | 81.2(8) | O3-In1-O1 | 77.6(4) |
| O1-In1-O1 | 94.9(7) | O5-Cd1-O6 | 94.6(7) |
| O3-In1-O1 | 77.6(4) | O6-Cd1-O2 | 83.4(6) |
| O5-Cd1-O2 | 176.2(8) | O6-Cd1-O4 | 164.8(5) |
| O5-Cd1-O4 | 100.5(7) | O5-Cd1-O6 | 97.5(7) |
| O2-Cd1-O4 | 81.4(6) | O2-Cd1-O6 | 86.0(5) |
| O6-Cd1-O6 | 98.2(6) | O5-Cd1-O4 | 97.4(7) |
| O4-Cd1-O6 | 80.5(5) | O2-Cd1-O4 | 79.1(5) |
| O6-Cd1-O4 | 81.7(5) | O6-Cd1-O4 | 165.0(5) |
| O4-Cd1-O4 | 95.7(5) | O3-Cd2-O3 | 96.9(5) |
| O3-Cd2-O4 | 109.0(5) | O3-Cd2-O4 | 103.5(5) |
| O3-Cd2-O2 | 92.3(5) | O3-Cd2-O2 | 170.0(5) |
| O4-Cd2-O2 | 77.0(5) | O3-Cd2-O6 | 119.8(5) |
| O3-Cd2-O6 | 91.2(5) | O4-Cd2-O6 | 126.7(5) |
| O2-Cd2-O6 | 80.7(5) | O3-Cd2-O2 | 176.0(5) |
| O3-Cd2-O2 | 84.9(5) | O4-Cd2-O2 | 73.9(5) |
| O2-Cd2-O2 | 85.7(5) | O6-Cd2-O2 | 56.5(5) |
| O3-B1-O6 | 123.6(19) | O3-B1-O2 | 119.3(19) |
| O6-B1-O2 | 117.1(17) | O4-B2-O1 | 120.5(15) |

| O4-B2-O4 | 119.(3) | O4-B2-O1 | 120.5(15) |

**Table S5.** Dipole moments of $BO_3$ and $CdO_n$ (n =6, 8) polyhedra in the unit cell.

| Species | | a-axis (D) | b-axis (D) | c-axis (D) | total (D) |
|---|---|---|---|---|---|
| Cd$_4$InO(BO$_3$)$_3$ | BO$_3$ | 0 | 1.025 | 0 | 1.025 |
| | CdO$_n$ (n=6,8) | 0 | 0.878 | 0 | 0.878 |
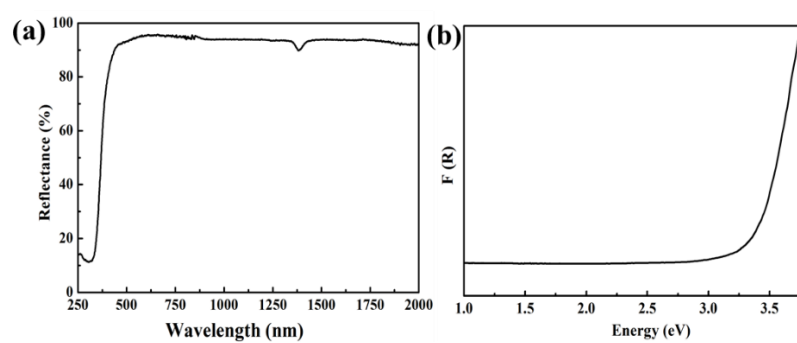
**Figure S1.** The UV-Vis-NIR diffuse reflectance spectroscopy of $Cd_4InO(BO_3)_3$.

**Figure S2.** The IR spectroscopy of $Cd_4InO(BO_3)_3$.

**Table S6.** The assignments of the Infrared absorption peaks for CIBO

| Type of vibration | characteristic absorption peak ($cm^{-1}$) of CIBO |
|---|---|
| $B_3$-O asymmetric stretching vibration | 1174 |
| $B_3$-O symmetrical stretching vibration | 933 |
| $B_3$-O Out-of-plane bending vibration | 707 |
| $B_3$-O bending vibration | 583 |

Table S7. The PXRD pattern of CIBO

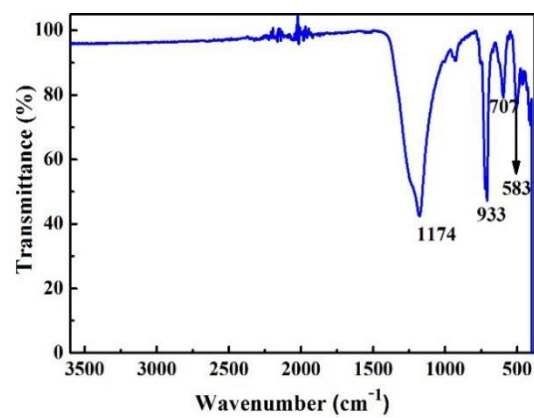| 2-Theta | d | BG | Height | I % | Area | I% | FWHM | XS |
|---|---|---|---|---|---|---|---|---|
| 12.697 | 6.9659 | 1 | 286 | 2.9 | 2013 | 2.4 | 0.12 | >1000 |
| 20.381 | 4.3539 | 12 | 5233 | 52.5 | 36663 | 42.9 | 0.119 | >1000 |
| 22.538 | 3.9418 | 13 | 1162 | 11.7 | 10027 | 11.7 | 0.147 | 755 |
| 22.879 | 3.8837 | 9 | 2547 | 25.6 | 18659 | 21.8 | 0.125 | >1000 |
| 25.542 | 3.4846 | 7 | 3755 | 37.7 | 26720 | 31.3 | 0.121 | >1000 |
| 26.663 | 3.3405 | 6 | 459 | 4.6 | 3332 | 3.9 | 0.123 | >1000 |
| 27.722 | 3.2153 | 6 | 201 | 2 | 1277 | 1.5 | 0.108 | >1000 |
| 29.017 | 3.0747 | 6 | 1291 | 13 | 9445 | 11.1 | 0.124 | >1000 |
| 30.562 | 2.9227 | 25 | 7679 | 77.1 | 54782 | 64.1 | 0.121 | >1000 |
| 31.441 | 2.8429 | 286 | 7046 | 70.7 | 43172 | 50.5 | 0.104 | >1000 |
| 32.118 | 2.7845 | 40 | 9960 | 100 | 85445 | 100 | 0.146 | 779 |
| 32.322 | 2.7675 | 32 | 4912 | 49.3 | 42584 | 49.8 | 0.147 | 764 |
| 34.1 | 2.6271 | 45 | 2273 | 22.8 | 16496 | 19.3 | 0.123 | >1000 |
| 35.101 | 2.5544 | 17 | 2648 | 26.6 | 32011 | 37.5 | 0.206 | 464 |
| 35.417 | 2.5323 | 9 | 2201 | 22.1 | 17964 | 21 | 0.139 | 867 |
| 38.479 | 2.3376 | 2 | 242 | 2.4 | 2667 | 3.1 | 0.187 | 531 |
| 38.738 | 2.3226 | 3 | 1215 | 12.2 | 9239 | 10.8 | 0.129 | >1000 |
| 39.582 | 2.275 | 54 | 2839 | 28.5 | 18612 | 21.8 | 0.111 | >1000 |
| 40.199 | 2.2415 | 16 | 839 | 8.4 | 6793 | 8 | 0.138 | 894 |
| 40.541 | 2.2233 | 16 | 113 | 1.1 | 790 | 0.9 | 0.119 | >1000 |
| 41.442 | 2.177 | 19 | 703 | 7.1 | 5218 | 6.1 | 0.126 | >1000 |
| 41.702 | 2.1641 | 14 | 572 | 5.7 | 4993 | 5.8 | 0.148 | 775 |
| 42.381 | 2.131 | 8 | 400 | 4 | 2715 | 3.2 | 0.115 | >1000 |
| 43.798 | 2.0653 | 12 | 1568 | 15.7 | 10780 | 12.6 | 0.117 | >1000 |
| 45.041 | 2.0111 | 13 | 1150 | 11.5 | 8547 | 10 | 0.126 | >1000 |
| 45.277 | 2.0012 | 12 | 284 | 2.9 | 4145 | 4.9 | 0.248 | 379 |
| 46 | 1.9714 | 10 | 69 | 0.7 | 382 | 0.4 | 0.094 | >1000 |
| 46.739 | 1.9419 | 13 | 345 | 3.5 | 2119 | 2.5 | 0.104 | >1000 |
| 47.523 | 1.9117 | 19 | 725 | 7.3 | 4687 | 5.5 | 0.11 | >1000 |
| 48.416 | 1.8785 | 23 | 871 | 8.7 | 6388 | 7.5 | 0.125 | >1000 |
| 48.996 | 1.8576 | 25 | 53 | 0.5 | 355 | 0.4 | 0.114 | >1000 |
| 49.802 | 1.8294 | 27 | 2769 | 27.8 | 22821 | 26.7 | 0.14 | 892 |
| 49.979 | 1.8233 | 27 | 1171 | 11.8 | 14890 | 17.4 | 0.216 | 457 |
| 51.279 | 1.7801 | 28 | 2022 | 20.3 | 20862 | 24.4 | 0.175 | 612 |
| 51.979 | 1.7578 | 26 | 1029 | 10.3 | 9207 | 10.8 | 0.152 | 771 |
| 52.323 | 1.7471 | 27 | 1812 | 18.2 | 16734 | 19.6 | 0.157 | 731 |
| 53.563 | 1.7095 | 27 | 1037 | 10.4 | 7626 | 8.9 | 0.125 | >1000 |
| 53.96 | 1.6979 | 33 | 1180 | 11.8 | 10479 | 12.3 | 0.151 | 788 |
| 54.402 | 1.6851 | 26 | 1869 | 18.8 | 13477 | 15.8 | 0.123 | >1000 |
| 55.48 | 1.6549 | 26 | 913 | 9.2 | 5824 | 6.8 | 0.108 | >1000 |
| 56.262 | 1.6337 | 27 | 258 | 2.6 | 1468 | 1.7 | 0.097 | >1000 |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| 56.681 | 1.6226 | 21 | 123 | 1.2 | 1026 | 1.2 | 0.142 | 898 |
| 57.058 | 1.6128 | 20 | 508 | 5.1 | 5329 | 6.2 | 0.178 | 612 |
| 57.22 | 1.6086 | 19 | 367 | 3.7 | 5924 | 6.9 | 0.274 | 354 |
| 57.938 | 1.5904 | 17 | 124 | 1.2 | 691 | 0.8 | 0.095 | >1000 |
| 58.478 | 1.577 | 15 | 274 | 2.8 | 1916 | 2.2 | 0.119 | >1000 |
| 58.803 | 1.569 | 18 | 171 | 1.7 | 3164 | 3.7 | 0.315 | 306 |
| 59.098 | 1.5619 | 18 | 1186 | 11.9 | 11096 | 13 | 0.159 | 738 |
| 59.762 | 1.5461 | 29 | 1549 | 15.6 | 10735 | 12.6 | 0.118 | >1000 |
| 60.122 | 1.5377 | 29 | 316 | 3.2 | 3742 | 4.4 | 0.201 | 525 |
| 60.739 | 1.5236 | 40 | 100 | 1 | 444 | 0.5 | 0.075 | >1000 |
| 61.082 | 1.5158 | 28 | 311 | 3.1 | 2960 | 3.5 | 0.162 | 725 |
| 61.323 | 1.5105 | 28 | 797 | 8 | 7718 | 9 | 0.165 | 706 |
| 61.877 | 1.4983 | 17 | 233 | 2.3 | 2434 | 2.8 | 0.178 | 631 |
| 62.261 | 1.4899 | 17 | 741 | 7.4 | 5574 | 6.5 | 0.128 | >1000 |
| 63.219 | 1.4697 | 16 | 636 | 6.4 | 4123 | 4.8 | 0.11 | >1000 |
| 63.622 | 1.4613 | 19 | 74 | 0.7 | 976 | 1.1 | 0.224 | 466 |
| 63.962 | 1.4544 | 7 | 430 | 4.3 | 6538 | 7.7 | 0.258 | 393 |
| 64.421 | 1.4451 | 8 | 327 | 3.3 | 2927 | 3.4 | 0.152 | 819 |
| 65.383 | 1.4261 | 13 | 59 | 0.6 | 304 | 0.4 | 0.088 | >1000 |
| 65.624 | 1.4215 | 16 | 78 | 0.8 | 487 | 0.6 | 0.106 | >1000 |
| 66.24 | 1.4098 | 16 | 752 | 7.6 | 5609 | 6.6 | 0.127 | >1000 |
| 67.162 | 1.3926 | 19 | 776 | 7.8 | 5395 | 6.3 | 0.118 | >1000 |
| 67.777 | 1.3815 | 22 | 355 | 3.6 | 4830 | 5.7 | 0.231 | 459 |
| 68.02 | 1.3771 | 12 | 222 | 2.2 | 2098 | 2.5 | 0.161 | 762 |
| 68.301 | 1.3722 | 12 | 309 | 3.1 | 2894 | 3.4 | 0.159 | 775 |
| 68.736 | 1.3645 | 8 | 58 | 0.6 | 476 | 0.6 | 0.14 | 989 |
| 69.321 | 1.3544 | 10 | 122 | 1.2 | 1192 | 1.4 | 0.166 | 728 |
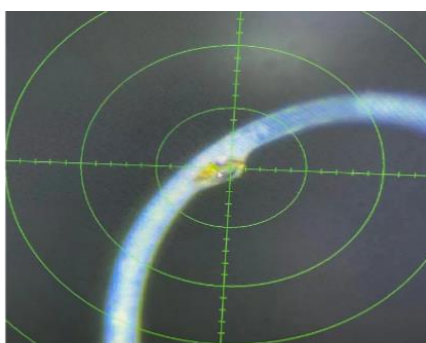
**Figure S3.** Crystal for the birefringence determination