JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

High quality. High impact.

Journal of the American Chemical Society is published by the American Chemical Society. 1155 Sixteenth Street N.W., Washington, DC 20036

J|A|C|S
COMMUNICATIONS

$Se_2(B_2O_7)$: A New Type of Second-Order NLO Material

Fang Kong, Shu-Ping Huang, Zhong-Ming Sun, Jiang-Gao Mao,* and Wen-Dan Cheng*

State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter,
Chinese Academy of Sciences, Fuzhou 350002, P. R. China

Received March 27, 2006; E-mail: mjg@fjirsm.ac.cn; cwd@fjirsm.ac.cn

Second-order nonlinear optical (NLO) materials are of current interest and great importance owing to their uses in photonic technologies.[1] The most widely used such materials at present are mainly inorganic crystals based on borates, such as β-BaB_2O_4 (BBO) and LiB_3O_5 (LBO), and phosphates, such as KH_2PO_4 (KDP) and $KTiOPO_4$ (KTP).[2] It is reported that the active groups responsible for the NLO properties in BBO and LBO crystals are $(B_3O_6)^{3-}$ and $(B_3O_7)^{5-}$ anions, respectively. Metal borophosphates containing both borate and phosphate groups are also promising NLO materials.[3] The asymmetric coordination polyhedron adopted by Se^{IV} or Te^{IV} atoms is also reportedly able to afford noncentrosymmetric structures with consequent interesting physical properties, such as nonlinear optical second harmonic generation (SHG).[4−6] Transition metal ions with d^0 electronic configuration, such as Ti^{4+}, Nb^{5+}, W^{6+}, and Mo^{6+}, etc., which are susceptible to second-order Jahn−Teller distortions, have been introduced to the metal selenite or tellurite systems in order to enhance their SHG properties.[4−6] We deem that a compound containing both borate anion and selenium(IV) or tellurium(IV) which contains the lone pair electrons may possess good SHG properties due to the presence of two types of SHG active groups. So far, no such compounds have been reported. Our exploration on the compounds in the selenite−borate system led to the discovery of a new second-order NLO material, $Se_2B_2O_7$, with a SHG efficiency of about 2.2 times that of KDP (KH_2PO_4) based on powder SHG measurements. Herein we report its synthesis, crystal structure, and optical properties.

Single crystals of $Se_2B_2O_7$ were isolated quantitatively by the solid-state reaction of B_2O_3 (1.2 mmol) and SeO_2 (2.4 mmol) at 320 °C in an evacuated quartz tube. Its purity was confirmed by XRD powder diffraction studies. The measured XRD powder pattern matches the one simulated from single-crystal X-ray diffraction studies.[7] $Se_2B_2O_7$ is slightly moisture sensitive in air at room temperature.

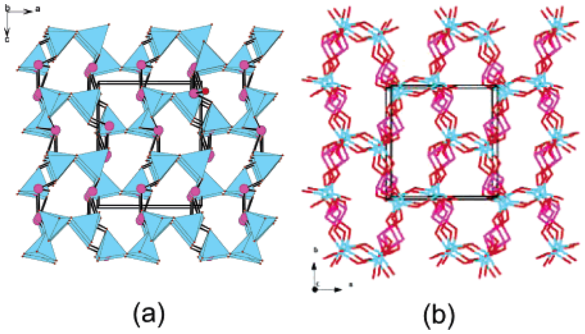

Figure 1. View of the structure of $Se_2B_2O_7$ down the *b* axis (a) and wire representation of the structure of $Se_2B_2O_7$ down the *c* axis (b). BO_4 tetrahedra are shaded in cyan. Se, B, and O atoms are drawn as pink, cyan, and red circles, respectively.

The structure of $Se_2B_2O_7$ features a 3D network composed of $B_2O_7^{8-}$ anions interconnected by Se^{IV} atoms (Figure 1). The boron atoms are tetrahedrally coordinated by four oxygen atoms, which is different from the trigonal BO_3 geometry in BBO.[2b] In LBO, both trigonal BO_3 and tetrahedral BO_4 groups are found.[2c] A pair of BO_4 tetrahedra are further interconnected into a $B_2O_7^{8-}$ unit via corner sharing (O(7)). The B−O distances range from 1.40(1)−1.516(9) Å and O−B−O bond angles fall in the range of 102.8(6)−117.5(6)°. These bond lengths and angles are comparable to those in other borates.[2,3] The B(1)−O(7)−B(2) angle is 130.7(5)°. In BBO, three BO_3 groups are corner-sharing to form a planar $(B_3O_6)^{3-}$ unit, whereas in LBO, the interconnection of planar BO_3 and tetrahedral BO_4 groups resulted in a 3D network with large tunnels occupied by lithium atoms.[2] Both Se(1) and Se(2) adopt a ψ-SeO_3 trigonal pyramidal geometry with the lone pair electrons occupying the pyramidal sites. The Se−O distances are in the range of 1.695(5)−1.709(5) Å, which are comparable to those reported in other metal selenites.[8] Bond valence calculations indicate that the B atoms are in an oxidation state of +3 and the Se atoms are +4, the calculated total bond valences for B(1), B(2), Se(1), and Se(2) are 3.03, 3.04, 4.01, and 3.96, respectively.[9]

The open framework of $Se_2B_2O_7$ can also be described as an interesting mixed (3,4)-connected net of the B and Se (linked by −O− bridges) (Figure 1). Such net is the ins-type which has been reported in InS and silver complex of hexamethylenetetramine.[10] Right-handed helical tunnels along the *c* axis are formed (Figure 1b). These tunnels are based on B_6Se_4 10-membered rings. The lone pairs of the Se^{IV} atoms are orientated toward the above tunnels.

TGA studies show that there is only very slight weight loss before 300 °C, which is due to the release of the surface water absorbed. Then it exhibits a large step of weight loss which is completed at 440 °C, which corresponds to the release of two molecules of SeO_2 per formula unit. The final residuals are B_2O_3. The total weight loss of 75.7% is in good agreement with the theoretical value of 76.1%.

The noncentrosymmetric structure of $Se_2B_2O_7$ prompts us to measure its SHG properties. SHG measurements on the powder samples reveal that $Se_2B_2O_7$ exhibits a SHG efficiency of about 2.2 times that of KDP (KH_2PO_4). Further absorption spectrum measurements indicate that $Se_2B_2O_7$ is transparent in the range of 400−2000 nm. From 400 to 190 nm, the absorption increases with the decreasing wavelength, and the largest absorption rate is about 23% at 190 nm. Hence $Se_2B_2O_7$ can be used in UV, visible, and near-IR regions as a NLO material. Optical diffuse reflectance study of $Se_2B_2O_7$ reveals an optical band gap of 4.64 eV (see Supporting Information); therefore, $Se_2B_2O_7$ is a wide band gap semiconductor. For comparison, the band gaps for BBO (6.43 eV) and LBO (7.78 eV) are much wider.[11]

To gain further insights on the band structure and optical properties of $Se_2B_2O_7$, band structure and optical property calculations for $Se_2B_2O_7$ were performed by using the total-energy code CASTEP.[12]

10.1021/ja0620991 CCC: $33.50 © 2006 American Chemical Society

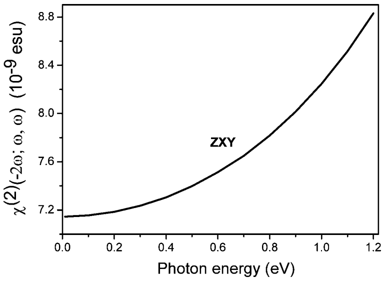

Figure 2. Calculated dynamic second-order susceptibilities of $Se_2B_2O_7$.

Results of band structure calculations indicate that $B_2Se_2O_7$ is an indirect gap semiconductor with a band gap of 3.99 eV, which is slightly smaller than that derived from optical diffuse reflectance spectrum study. The band just above the Fermi level is predominately derived from unoccupied Se-4p and O-2p states. The band just below the Fermi level is composed of O-2p, Se-4p, and B-2p states, mixing with small amounts of Se-4s, O-2s, and B-2s states.

The calculations of linear optical properties described in terms of the complex dielectric function $\epsilon(\omega) = \epsilon_1(\omega) + i\epsilon_2(\omega)$ were made. The imaginary part of the dielectric function ϵ_2 was given in the following equation:[13]

$$\epsilon_2^{ij}(\omega) = 8\pi^2\hbar^2e^2/(m^2V)\sum_k\sum_{cv}(f_c - f_v)^{p^i_{cv}(k)p^j_{vc}(k)}/_{(E^2_{vc})}\delta[E_c(k) - E_v(k) - \hbar\omega] \quad (1)$$

The first-order susceptibility and the linear refractive index can be derived from the dielectric function. The first-order nonresonant susceptibility at the low frequency region is given by $\chi^{(1)}(\omega)_{ii} = [\epsilon(\omega)_{ii} - 1]/4\pi$, and the second-order susceptibilities can be expressed in terms of the first-order susceptibilities as follows:[14]

$$\chi^{(2)}_{ijk}(-\omega_3;\omega_1,\omega_2) = F^{(2)}\chi^{(1)}_{ii}(\omega_3)\chi^{(1)}_{jj}(\omega_1)\chi_{kk}{}^{(1)}(\omega_2) \qquad (2)$$

where $F^{(2)} = ma/(N^2e^3)$. These expressions are derived from a classical anharmonic oscillator (AHO) model. The m and e are, respectively, the electron mass and charge, and the parameters a, characterizing the nonlinearity of the response, can be obtained from experimental or theoretical estimations. It is noted that N is a density number of unit cells in a crystal instead of density number of atoms in a classical AHO model.

The dielectric functions of orthorhombic structured $B_2Se_2O_7$ are resolved into three components: $\epsilon_x(\omega)$, which is the spectrum for polarization along a direction ($E \parallel a$ axis), $\epsilon_y(\omega)$ ($E \parallel b$ axis), and $\epsilon_z(\omega)$ ($E \parallel c$ axis). The average function, $\epsilon_2(\omega)$, is given as $(\epsilon_{2x} + \epsilon_{2y} + \epsilon_{2z})/3$ (see Supporting Information). The most prominent peak is located at 6.1 eV, which mainly originates from the O-2p to Se-4p direct interband transitions. The average value of polarized zero frequency dielectric constants is $\epsilon(0) = (\epsilon_x + \epsilon_y + \epsilon_z)/3 = 2.03$. The dispersion of linear refractive index displays strong anisotropy which arises from the anisotropy of the dielectric function, $n^c > n^b > n^a$, but n^c and n^b are much larger than n^a (see Supporting Information). $B_2Se_2O_7$ belongs to the crystal class 222. According to Kleinman's symmetry conditions, only one independent component ZXY exists. The frequency-dependent (dynamic) second-order susceptibilities of $\chi^{(2)}(-2\omega, \omega, \omega)_{zxy}$ calculated by eq 2 is shown in Figure 2. The calculated value of d_{36} ($d = 1/2\chi^{(2)}$) is about 4.36×10^{-9} esu, at a wavelength of 1064 nm (1.165 eV), which is nearly 4 times that of KDP ($d_{36} = 1.1 \times 10^{-9}$ esu). This value is significantly higher than our measurements on powder samples as the calculations are based on single crystals that generate much stronger SHG signals under phase-matching considerations.

In summary, the combination of the lone pair containing selenium(IV) and borate anion resulted in $Se_2B_2O_7$ with good SHG property. Our future efforts will be devoted to the growth of large crystals and related physical property studies for this compound. We will also explore other similar systems to find other new NLO materials.

Acknowledgment. We thank the Nation Natural Science Foundation of China (Nos. 20573113, 20371047, and 20521101) and NSF of Fujian Province (No. E0420003) for the financial support. We thank Prof. Ding Li for his great help with the SHG measurements.

Supporting Information Available: Details of crystallographic studies, physical property measurements, and theoretical calculations for $Se_2B_2O_7$ (in PDF and CIF format). This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) Chen, C.; Liu, G. *Annu. Rev. Mater. Sci.* **1986**, *16*, 203−243.
(2) (a) Becker, *P. Adv. Mater.* **1998**, *10*, 979−992. (b) Chen, C.-T.; Wang, Y.-B.; Wu, B.-C.; Wu, K.-C.; Zeng, W.-L.; Yu, L.-H. *Nature* **1995**, *373*, 322−324. (c) Chen, C.-T.; Wu, B.-C.; Jiang, A. D.; You, G. M. *Sci. Sin., Ser B* **1985**, *28*, 235−243. (d) Chen, C.-T.; Wu, Y.; Jiang, A. D.; Wu, B.-C.; You, G.; Li, R.; Lin, S. *J. Opt. Soc. Am. B* **1989**, *6*, 616−621.
(3) (a) Pan, S.; Wu, Y.-C.; Fu, P.-Z.; Zhang, G.-C.; Li, Z.-H.; Du, C. X.; Chen, C.-T. *Chem. Mater.* **2003**, *15*, 2218−2221. (b) Li, Z.-H.; Lin, Z.-S.; Wu, Y.-C.; Fu, P. Z.; Wang, Z. Z.; Chen, C. T. *Chem. Mater.* **2004**, *16*, 2906−2908.
(4) (a) Ra, H.-S.; Ok, K.-M.; Halasyamani, P. S. *J. Am. Chem. Soc.* **2003**, *125*, 7764. (b) Ok, K.-M.; Halasyamani, P. S. *Inorg. Chem.* **2004**, *43*, 4248.
(5) (a) Hart, R. T.; Ok, K.-M.; Halasyamani, P. S.; Zwanziger, J. W. *Appl. Phys. Lett.* **2004**, *85*, 938−939. (b) Goodey, J.; Broussard, J.; Halasyamani, P. S. *Chem. Mater.* **2002**, *14*, 3174−3180.
(6) (a) Johnston, M. G.; Harrison, W. T. A. *Inorg. Chem.* **2001**, *40*, 6518−6520. (b) Balraj, V.; Vidyasagar, K. *Inorg. Chem.* **1999**, *38*, 5809−5813.
(7) Crystal data for $Se_2B_2O_7$: $M_r = 291.54$, orthorhombic, $P2_12_12_1$ with $a = 7.4815(6)$ Å, $b = 7.8984(5)$ Å, $c = 9.0478(7)$ Å, $V = 534.65(7)$ Å^3, $Z = 4$. The final least-squares refinements converged at $R1$ ($wR2$) = 0.0416 (0.0708) and $S = 1.158$ for 1269 reflections with $I > 2\sigma(I)$.
(8) (a) Shen, Y.-L.; Jiang, H.-L.; Xu, J.; Mao, J.-G.; Cheah, K.-W. *Inorg. Chem.* **2005**, *44*, 9314−9321. (b) Shen, Y.-L.; Mao, J.-G. *Inorg. Chem.* **2005**, *44*, 5328−5335. (c) Johnsson, M.; Törnroos, K. W.; Mila, F.; Millet, P. *Chem. Mater.* **2000**, *12*, 2853−2857. (d) Johnsson, M.; Törnroos, K. W.; Lemmens, P.; Millet, P. *Chem. Mater.* **2003**, *15*, 68−73.
(9) (a) Brown, I. D.; Altermatt, D. *Acta Crystallogr.* **1985**, *B41*, 244−247. (b) Brese, N. E.; O'Keeffe, M. *Acta Crystallogr.* **1991**, *B47*, 192−197.
(10) (a) Walther, R.; Deiseroth, H. J. *Z. Kristallogr.* **1995**, *210*, 360. (b) Carlucci, L.; Ciani, G.; Gudenberg, D. W.; Proserpio, D. M.; Sironi, A. *Chem. Commun.* **1997**, 631−632.
(11) French, R. H.; Ling, J. W.; Ohuchi, F. S.; Chen, C. T. *Phys. Rev. B* **1991**, *44*, 8496−8502.
(12) (a) Segall, M. D.; Lindan, P. L. D.; Probert, M. J.; Pickard, C. J.; Hasnip, P. J.; Clark, S. J.; Payne, M. C. *J. Phys.: Condens. Matter* **2002**, *14*, 2717−2743. (b) Milman, V.; Winkler, B.; White, J. A.; Pickard, C. J.; Payne, M. C.; Akhmatskaya, E. V.; Nobes, R. H. *Int. J. Quantum Chem.* **2000**, *77*, 895−910.
(13) Bassani, F.; Parravicini, G. P. *Electronic States and Optical Transitions In Solids*; Pergamon Press Ltd.: Oxford, 1975; pp 149−154.
(14) Boyd, R. W. *Nonlinear Optics*; Academic Press: New York, 1992; pp 21−32.

JA0620991