Inorg. Chem. **2006**, *45*, 6840–6843

Inorganic Chemistry

Article

$Ba_4Ga_2B_8O_{18}Cl_2$·NaCl: A New Polar Structure with NaCl Inclusion

R. K. Li* and Yi Yu

Technical Institute of Physics and Chemistry, Chinese Academy of Sciences,
Beijing 100080, China

Received May 9, 2006

The title compound, $Ba_4Ga_2B_8O_{18}Cl_2$·NaCl, is found to crystallize in a polar space group $P4_2nm$ with cell dimensions of $a = 12.1134(2)$ Å and $c = 6.8456(1)$ Å. The basic building blocks of the structure are the B_4O_9 groups, which are interconnected by the GaO_4 tetrahedron to form a three-dimensional net with Ba^{2+} ion-, Cl^- ion-, and NaCl molecule-filled tunnels. This net structure is closely related to that of mineral hilgardite, with which many variant compounds have been found. Both a powder second-harmonic-generation test and calculations suggest that it possesses an optical nonlinearity comparable to that of potassium dihydrogen phosphate.

Introduction

Compounds with polar structures have found many applications as piezoelectric, pyroelectric, ferroelectric, electro-optical, and nonlinear optical (NLO) materials. It is always a challenge to discover new materials with polar structures to fulfill technical requirements. Design strategies including modifying known polar structures, for example, the boracite and hilgardite families,[1,2] and, more recently, the inclusion of an asymmetric salt unit as a template have been proved to be fruitful in obtaining polar solids.[3] Boracite and its derivatives were found to be the first multiferroic materials and have been paid reviving interest in recent years.[4] A large nonlinear optical effect was also discovered in a member of the hilgardite family.[5] Besides boracites and hilgardites, many polar structures have also been found in borate compounds with a great number of structure variations because boron atoms can coordinate to both three and four oxygens and tend to form polyanions. In recent decades, good and widely applied nonlinear optical crystals have also been developed in borate compounds, which include BaB_2O_4 (BBO),[6] LiB_3O_5 (LBO),[7] CsB_3O_5 (CBO),[8] and $KBe_2BO_3F_2$ (KBBF).[9] In our continued interest in searching for new NLO materials, when the Ga-substituted Ba-hilgardite was prepared with a NaCl flux, the title compound with a new polar structure type that related to hilgardite was found.

Experimental Section

Synthesis. The title compound, $Ba_4Ga_2B_8O_{18}Cl_2$·NaCl, was prepared from a stoichiometric ratio of analytically pure chemicals of $BaCO_3$, $BaCl_2$·$2H_2O$, NaCl, Ga_2O_3, and H_3BO_3. The starting materials were thoroughly ground and placed in a Pt crucible and then slowly (5 °C/h) heated to 500 °C. The sample was then cooled and ground again and fired at 800−850 °C for 5 days. This last step was repeated several times until the final product showed no changes when checked by X-ray diffraction.

Crystallographic Studies. The structure of the title compound was determined ab initio from powder X-ray diffraction (XRD) data (Figure 1) collected on a Siemens D-5000 diffractometer with a monochromated Cu Kα_1 radiation source ($\lambda = 1.540\,56$ Å). The data were collected in the 2θ range of 5−109° with a step size of 0.02° and a counting time of 3 s per step. A total of 129 well-resolved XRD peaks were found and can be indexed by a tetragonal lattice, and these were then fed to the program Checkcell,[10] which proposed a noncentrosymmetric space group $P4_2nm$, consistent with

---

* To whom correspondence should be addressed. E-mail: rkli@cl.cryo.ac.cn.

(1) (a) Nelmes, R. J. *J. Phys. C: Solid State Phys.* **1974**, *7*, 3840−54 and references therein. (b) Schmid, H. *J. Phys. Chem. Solids* **1965**, *26*, 973−6.

(2) (a) Fouassier, C.; Levasseaur, A.; Hagenmuller, P. *J. Solid State Chem.* **1971**, *3*, 206−12. (b) Peters, T. E.; Baglio, J. *J. Inorg. Nucl. Chem.* **1970**, *32*, 1089−96.

(3) (a) Etheredge, K. M. S.; Hwu, S. J. *Inorg. Chem.* **1995**, *34*, 3123−25. (b) Huang, Q.; Hwu, S.-J. *Inorg. Chem.* **2003**, *42*, 655−657. (c) Mo, X. H.; Hwu, S. J. *Inorg. Chem.* **2003**, *42*, 3978−80. (d) Mo, X. H.; Ferguson, E.; Hwu, S. J. *Inorg. Chem.* **2005**, *44*, 3121−6.

(4) Ascher, E.; Rieder, H.; Schmid, H.; Stössel, H. *J. Appl. Phys.* **1966**, *37*, 1404−5. Castellanos-Guzman, A. G.; Trujillo-Torrez, M.; Czank, M. *Mater. Sci. Eng., B* **2002**, *120*, 59−63.

(5) Belokoneva, E. L.; Kabalov, Y. K.; Dimitrova, O. V.; Stefanovich, S. Y. *Cryst. Rep.* **2003**, *48*, 44−8.

(6) Chen, C. T.; Wu, B. C.; Jiang, A. D.; You, G. M. *Sci. Sin., Ser. B* **1985**, *28*, 235−243.

(7) Chen, C. T.; Wu, Y. C.; Jiang, A. D.; Wu, B. C.; You, G. M.; Li, R. K.; Lin, S. J. *J. Opt. Soc. Am. B* **1989**, *6*, 616−621.

(8) Wu, Y. C.; Sasaki, T.; Nakai, S.; Yokotani, A.; Tang, H. G.; Chen, C. T. *Appl. Phys. Lett.* **1993**, *62*, 2614−5.

(9) Lu, J. H.; Wang, G. L.; Xu, Z. Y.; Chen, C. T.; Wang, J. Y.; Zhang, C. Q.; Liu , Y. G. *Opt. Commun.* **2001**, *200*, 415−8.

10.1021/ic060786n CCC: $33.50

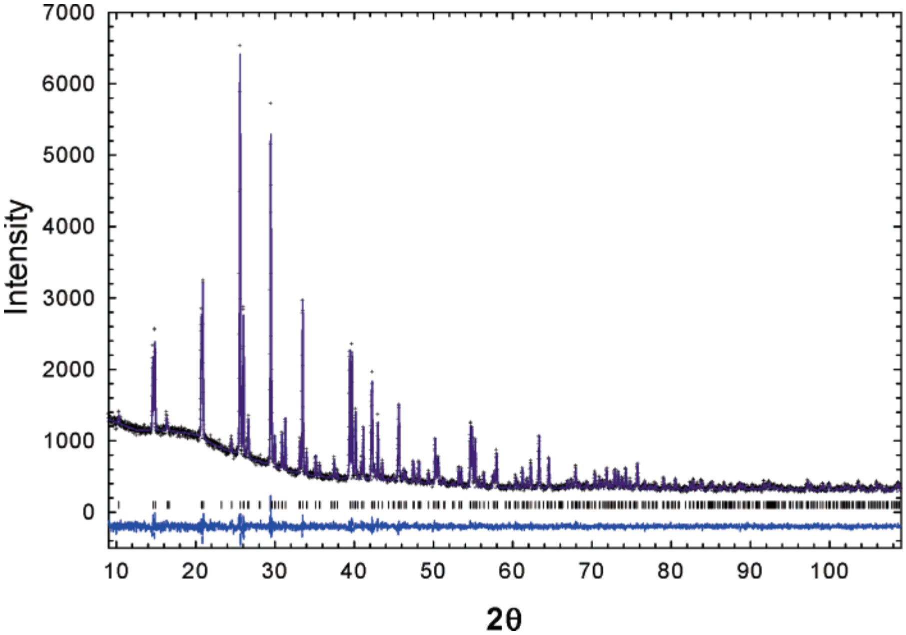

Figure 1. Rietveld refinement fit to the powder X-ray diffraction pattern of $Ba_4Ga_2B_8O_{18}Cl_2$·NaCl.

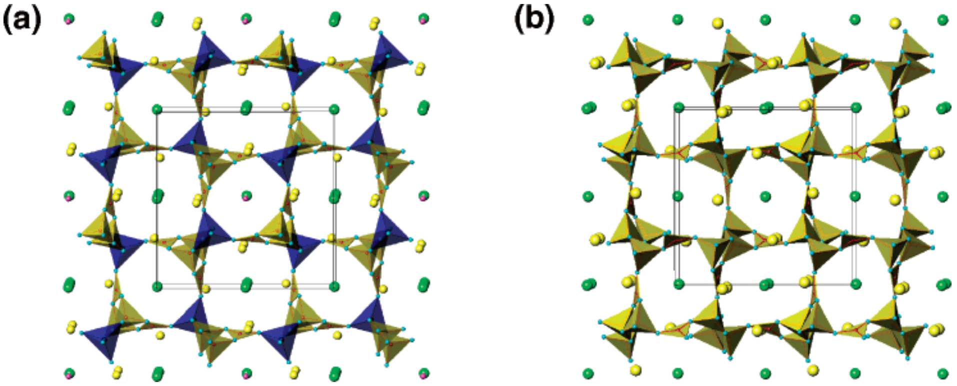

Figure 2. Comparison of crystal structures of (a) $Ba_4Ga_2B_8O_{18}Cl_2$·NaCl and (b) $Ba_2B_5O_9Cl$ viewed down the *ab* plane (blue tetrahedrons are GaO_4; BO_3 triangles and BO_4 tetrahedrons are yellow-colored; purple balls are Na; yellow balls are Ba, and green balls are Cl atoms).

the observation of a green light signal from the second harmonic generation (SHG) of a Nd:YAG laser with the powdered sample. Starting from this space group, a *le Bail* extraction[11] of the diffraction intensities was performed with the EXPGUI and GSAS program packages.[12] The starting structural model then was obtained by a direct method using SHELXS[13] from the extracted intensity; at the first stage, only four heavy atoms Ba, Ga, and Cl1, and Cl2 were found. Consequently, the positions of the remaining O atoms and Na atom were found one by one by difference Fourier synthesis with the Rietveld method using the GSAS program. The coordinates of the B atoms were idealized as the averages of the positions of (at roughly the center of) an O_3 triangle and two O_4 tetrahedra with edge lengths less than 2.55 Å. During the Rietveld refinement, it was found that the temperature factors of the Cl2 and Na atoms were abnormally high and became reasonable when refined together with their fractional occupancies, indicating an approximately 12−14% NaCl deficiency.

Results and Discussion

The structure of $Ba_4Ga_2B_8O_{18}Cl_2$·NaCl from the Rietveld refinement is shown in Figure 2a (see also the Supporting Information for additional data). The basic building block of the present compound is the B_4O_9 $[B_4O_5O_{4/2}]^{2-}$ group (Figure 3a), which is connected by sharing its four terminal oxygens with the GaO_4 group to form a three-dimensional (3D) $[GaB_4O_9]^{3-}$ net. The tetraborate B_4O_9 group is found in many anhydrous as well as hydrous borates. Depending on the amount of H saturation of the four terminal oxygens of the B_4O_9 group, it can exist as, for example, an isolated $[B_4O_5(OH)_4]^{2-}$ group in Borax $Na_2B_4O_5(OH)_4$·$8H_2O$,[14] as a $[B_4O_5O_{2/2}(OH)_2]^{2-}$ group with a $[MnB_4O_7(OH_2)]^{2-}$ chain in Roweite $Ca_2Mn_2(OH)_4B_4O_7(OH)_2$,[15] as an “isolated” B_4O_9

---

(10) Laugier, J.; Bochu, B. *CHECKCELL*; Laboratoire des Materiaux et du Génie Physique de l′Ecole Supérieure de Physique de Grenoble: Grenoble, France.

(11) Le Bail, A.; Duroy, H.; Fourquet, J. L. *Mater. Res. Bull.* **1988**, *23*, 447−52.

(12) Larson, A. C.; Von Dreele, R. B. *General Structure Analysis System (GSAS), 1994*; Los Alamos National Laboratory Report LAUR 86-748; Los Alamos National Laboratory: Los Alamos, NM, 1994. Toby, B. H. *J. Appl. Crystallogr*. **2001**, *34*, 210−3.

(13) Sheldrick, G. M. *SHELXS97*; University of Gottingen: Gottingen, Germany, 1997; *SHELXL97*; University of Gottingen: Gottingen, Germany, 1997.

(14) Levy, H. A.; Lisensky, G. C. *Acta Crystallogr., Sect. B* **1978**, *34*, 3502−10.

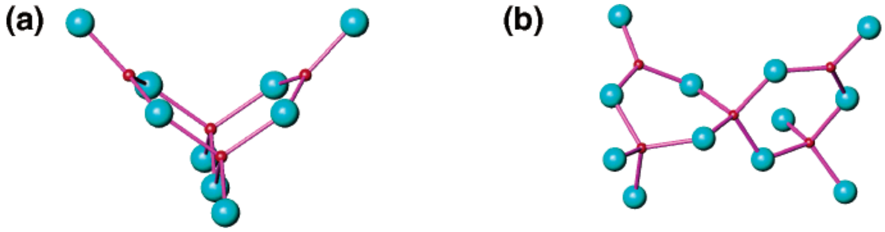

Figure 3. Comparison of the (a) B_4O_9 $[B_4O_5O_{4/2}]^{2-}$ and (b) B_5O_{12} $[B_5O_6O_{6/2}]^{3-}$ groups found in $Ba_4Ga_2B_8O_{18}Cl_2{\cdot}NaCl$ and $Ba_2B_5O_9Cl$.

Table 1. Atomic Parameters[a] of $Ba_4Ga_2B_8O_{18}Cl_2{\cdot}NaCl$

atom	site/occupancy	*x*	*y*	*z*	U_{iso}(Å^2) × 100
Ba	8d	0.51575(15)	0.22628(13)	0	1.05(6)
Ga	4c	0.2010(3)	0.2010(3)	0.001(3)	0.2(1)
Cl1	2a	0	0	0.563(2)	2.7(7)
Cl2	4b/0.94(2)	0.5	0	0.719(5)	6.1(8)
Na	2a/0.86(4)	0	0	0.166(5)	6.1(8)
O1	8d	0.4376(16)	0.2950(16)	0.655(3)	0.4(3)
O2	4c	0.2451(16)	0.2451(16)	0.587(3)	0.4(3)
O3	8d	0.3848(17)	0.2423(18)	0.324(3)	0.4(3)
O4	4c	0.3057(17)	0.6943(17)	0.756(5)	0.4(3)
O5	8d	0.5714(17)	0.2605(17)	0.3874(2)	0.4(3)
O6	4c	0.8001(15)	0.1999(15)	0.411(4)	0.4(3)
B1	8d	0.266	0.466	0.464	1.8
B2	4c	0.2666	0.2666	0.3728	1.8
B3	4c	0.3196	0.3196	0.7021	1.8

[a] Space group: $P4_2nm$, $a = 12.1134(2)$ Å, $c = 6.8456(1)$ Å, Rwp = 4.41%, $\chi^2 = 1.195$. Data without standard deviations are fixed during the refinement.

group in $Na_3GaB_4O_9$,[16] and as a 3D $[B_4O_5O_{4/2}]^{2-}$ net in $Li_2B_4O_7$.[17] Especially, similar to the present compound, in $Na_3GaB_4O_9$, the B_4O_9 group is also linked by sharing common oxygen atoms of the GaO_4 tetrahedral group to form a double layer. In this case, it may better be classified as a $[GaB_4O_9]^{3-}$ double layer rather than the isolated B_4O_9 group as originally proposed in ref 16.

The net structure of $Ba_4Ga_2B_8O_{18}Cl_2{\cdot}NaCl$ is closely related to that of the mineral hilgardite (e.g., $Ba_2B_5O_9Cl$;[18] Figure 2b). They differ in the basic building unit, which is B_5O_{12} in hilgardite, as compared to B_4O_9 in $Ba_4Ga_2B_8O_{18}Cl_2{\cdot}NaCl$. Remarkably, in the two compounds, both B_4O_9 and B_5O_{12} groups (Figure 3a,b) have two nearly perpendicular BO_3 triangular groups each with an unsaturated terminal oxygen B−O bond pointed in directions with an angle of 90° between them. Through sharing these terminal oxygen atoms, hilgardite (connected to another B_5O_{12} group) and the present compound (jointed by GaO_4 tetrahedra) form a square net in the *ab* plane with two types of tunnels. Within each unit cell, both tunnels in $Ba_2B_5O_9Cl$ host the same single Cl^- ions, whereas in $Ba_4Ga_2B_8O_{18}Cl_2{\cdot}NaCl$, the smaller one with 2-fold rotation symmetry hosts one Na^+ and one Cl^- ion, and the larger one with symmetry 4_2 hosts two Cl^- ions; consequently, the densities of the ion populations in the tunnels of the present compound are twice those of $Ba_2B_5O_9Cl$. Such a multi-ion population in the tunnels has also been observed in other compounds of the hilgardite family, for example, in $Ba_2B_5O_9Cl{\cdot}0.5H_2O$,[19] $Pb_2B_5O_9Cl{\cdot}0.5NaOH$,[20] and natural hilgardite $Ca_2B_5O_9Cl{\cdot}H_2O$.[21] Similar to the case in Ba-hilgardite, Ba ions coordinated to all six oxygen atoms equatorially, while different from hilgardite, in the apical positions, it coordinated to three Cl ions (instead of two Cl ions as in hilgardite) of which two are from the larger tunnel Cl2 site and one is from the smaller tunnel Cl1 site. Ba and Cl also form a square sublattice interpenetrating with the main net structure formed by $[GaB_4O_9]$. Down the *ac* and *bc* planes, Ba−Cl forms zigzag chains running through the *b* and *a* directions; similar chains can be found in other halide inclusion compounds.[3]

As mentioned above, during the refinement, it was found that the Na and Cl2 atoms have large thermal factors, either indicating diffuse positioned atoms or site deficiencies. When refined with the deficiency model, the results showed about 94% Cl2 and 86% Na site occupancies (which correspond to a 12% NaCl loss on the basis of a Cl2 site occupancy or a 14% NaCl loss on the basis of a Na site occupancy), see Table 1. What surprises us is that Cl2- and Na-deficient sites are not bonded; the Cl1 atom bonded to Na in the same tunnel behaves normally, but the one in the neighboring tunnel over 6 Å apart from Na has a large thermal factor and tends to show deficiency in the refinement. This behavior of NaCl loss shows a tendency toward Cl singly populated tunnels, which means, if the NaCl is completely removed, the occupancy of the two tunnels will become the same as the case in synthetic hilgardite (e.g., $Ba_2B_5O_9Cl$[18]). From the bond length calculation, it is found that the Na−O bond length of 2.597(20) Å (see Table 2) is significantly longer than the sum of their ionic radii (2.42 Å), whereas that of Na−Cl1 [2.72(4) Å] is much shorter than the sum (2.83 Å)

---

(15) Moore, P. B.; Araki, T. *Am. Mineral.* **1974**, *59*, 60−5.
(16) Becker, P.; Froehlich, R. *Z. Kristallogr.* **2001**, *216*, 31−2.
(17) Krogh-Moe, J. *Acta Crystallogr., Sect. B* **1968**, *24*, 179−81.
(18) Held, P.; Liebertz, J. Bohaty, L. *Z. Kristallogr.* **2002**, *217*, 463−4.
(19) Ferro, O.; Merlino, S.; Vinogradova, S. A.; Pushcharovskii, D. Y.; Dimitrova, O. V. *J. Alloys Compd.* **2000**, *305*, 63−71.
(20) Belokoneva, E. L.; Korchemkina, T. A.; Dimitrova O. V.; Stefanovich, S. Y. *Cryst. Rep.* **2000**, *45*, 744−53.
(21) Burns, P. C.; Hawthorne, F. C. *Acta Crystallogr., Sect. C* **1994**, *50*, 653−55.

Table 2. Selected Bond Lengths (Å) of $Ba_4Ga_2B_8O_{18}Cl_2 \cdot NaCl$

Ba−Cl1	3.349(3)	Ga−O4	1.752(26)
Ba−Cl2	3.354(19)	Ga−O5 × 2	1.813(21)
Ba−Cl2	3.130(16)	Ga−O6	1.806(26)
Ba−O1	2.678(20)		
Ba−O2	2.863(17)	B1−O1	1.396(22)
Ba−O3	2.736(20)	B1−O3	1.401(19)
Ba−O3′	3.284(21)	B1−O5	1.382(20).
Ba−O4	2.896(21)	B2−O2	1.514(23)
Ba−O5	2.768(17)	B2−O3 × 2	1.499(21)
Ba−O6	2.828(12)	B2−O4	1.474(28)
		B3−O1 × 2	1.495(20)
Na−O1	2.72(4)	B3−O2	1.499(26)
Na−Cl1 × 4	2.597(20)	B3−O6	1.467(28)

and also that in rock salt with a Na−Cl bond length of 2.82 Å. Such observation may indicate that, in the smaller tunnel, Na and Cl are more or less forms of the NaCl molecule, and because it is weakly bonded to the rest of the lattice with a bond valence sum[22] for Na of only 0.72+ and that for Cl1 of 0.92-, at elevated temperatures, the Na and Cl ions may become mobile and may be extruded under certain conditions to give microporous material.

It is known from our earlier studies[23] and has been widely accepted[24] that SHG coefficients of borate crystals can be calculated from the superposition of the microscopic second-order susceptibilities of their constituent boron−oxygen groups. Taking this approximation and neglecting the contribution from the GaO_4 group and those from Ba- and Na-coordinated polyhedra, we found that the contributions to the SHG coefficients from the two BO_4 groups have opposite signs and cancel out. Therefore, the obtained SHG tensors of $d_{33} = 0.62$ pm/V and $d_{31} = d_{32} = -0.31$ pm/V are nearly purely from the BO_3 group. Those calculated SHG coefficients are in fair agreement with the experimental observations of about twice the generated intensity at 532 nm from a Nd:YAG laser compared to that of potassium dihydrogen phosphate (KDP; $d_{36} = 0.39$ pm/V). Besides the borate skeleton, considering the atomic arrangements of the GaO_4 group and NaCl in $Ba_4Ga_2B_8O_{18}Cl_2 \cdot NaCl$, it can be found that their polar axes all point to the same direction and, hence, are in a favorable situation to generate a large dipole moment, leading to a large polaribility. The GaO_4 and NaCl may add up to the SHG coefficients, and more importantly, when an external electric field is applied, they will contribute cooperatively to a large part in piezoelectric and electro-optic effects.

Conclusion

We report a NaCl inclusion compound with a new type of polar structure closely related to the mineral hilgardite. The present compound shows comparable optical nonlinearity to that of KDP. In light of the variations of composition and structure of the mineral hilgardite, it can be expected that new compounds with a similar structure to the present one can be obtained through ion substitution and different salt or water inclusions. New materials with even larger optical nonlinearities as those found with Pb-hilgardite[5] can also be envisaged. As it contains large tunnels in all three directions, it may open new possibilities to microporous or ionic conducting materials[25] by the inclusion and extrusion of different salts, water, or small organic molecules.

Acknowledgment. We thank T. Zhou for helping to collect the XRD pattern and the Chinese Academy of Science for financial support. One of the authors (Y.Y.) was a visiting student at the early stage of the study from Tongji University, Shanghai, China.

Supporting Information Available: Structural data for the title compound (in .txt format). This material is available free of charge via the Internet at http://pubs.acs.org.

IC060786N

---

[22] Brown, I. D.; Altermatt, D. *Acta Crystallogr., Sect. B* **1985**, *41*, 244−7.

[23] Chen, C. T.; Wu, Y. C.; Li, R. K. *Int. Rev. Phys. Chem.* **1989**, *8*, 65−91; *J. Cryst. Growth* **1990**, *99*, 790−8.

[24] Becker, P. *Adv. Mater.* **1998**, *10*, 979−92.

[25] Jettschko, W.; Bither, T. A.; Bierstedt, P. E. *Acta Crystallogr., Sect. B* **1977**, *33*, 2767−75.