Inorganic Chemistry
Communication
pubs.acs.org/IC

Borate Fluoride and Fluoroborate in Alkali-Metal Borate Prepared by an Open High-Temperature Solution Method

Hongping Wu,[†] Hongwei Yu,[†] Qiang Bian,[†,‡] Zhihua Yang,[†] Shujuan Han,[†] and Shilie Pan*,[†]

[†]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

[‡]University of Chinese Academy of Sciences, Beijing 100049, China

Supporting Information

ABSTRACT: By incorporation of the largest-electronegativity F atoms into borate, two novel halogen-containing borates, $Li_6RbB_2O_6F$ and $K_3B_3O_3F_6$, have been synthesized. Interestingly, $Li_6RbB_2O_6F$ is the first borate fluoride in alkali-metal borate. Meanwhile, $K_3B_3O_3F_6$ appears to be the first confirmed alkali-metal fluoroborate crystal grown by a high-temperature solution in air.

The research about the relationship of structure−property plays an important role in the design of functional compounds. As is known to all, the property is governed by the crystal structure of the compound;[1,2] thus, the design and synthesis of new compounds with presupposed structures is challenging for material scientists and chemists. During the past years, many strategies and methods have been put forward to guide the synthesis of the new compounds. For example, Poeppelmeier et al. have successfully used oxyfluoride groups to create new polar materials.[3] Halasyamani et al. have focused on synthesizing new oxide materials that contain cations susceptible to second-order Jahn−Teller distortions,[4] that is, octahedrally coordinated d^0 transition metals (Ti^{4+}, Nb^{5+}, W^{6+}, etc.) and cations with a stereoactive lone pair (Pb^{2+}, Bi^{3+}, Se^{4+}, Te^{4+}, I^{5+}, etc.).[5] Yang's group has made great progress in the systems containing organic and transition-metal complex-templated aluminoborates or organically templated borogermanates.[6] Mao et al. have successfully reported a new series of borogermanates by high-temperature solid-state reactions.[7]

Recently, our and other groups have been aware that introducing halogen into borate is a fruitful method for exploring the functional materials.[8−11] For example, using standard Schlenk techniques in a purified argon atmosphere,[9] several lithium fluorooxoborates have been efficiently synthesized, which endows the window for potential applications in batteries and fuel cells. For nonlinear-optical (NLO) material, a series of halogen-containing beryllium borates $ABe_2BO_3F_2$ (A = K, Rb, Cs),[9a] and $MM'Be_2B_2O_6F$ (M = Na, M′ = Ca; M = K, M′ = Ca, Sr)[9b] were synthesized through molecular engineering design. Among them, $KBe_2BO_3F_2$ (KBBF) is the only practically usable deep-UV NLO material; the excellent property can be attributed to its special structure with a $[Be_2BO_3F_2]_\infty$ layer structure, which results in broad transparency and large birefringence. Also, other halogen-containing borates including $K_3B_6O_{10}Cl$,[10a] $Ba_4B_{11}O_{20}F$,[10b] $M_3B_6O_{11}F_2$ (M = Ba, Sr, Pb),[11] and $Li_3Ca_9(BO_3)_7{\cdot}2LiF$,[12] etc., in succession have also been reported in our group, and some of them are promising UV NLO crystals.

However, on the basis of different connection modes between B and X (X = F, Cl, Br) atoms, the halogen-containing borate can be classified as two types: (1) borate halide, halide, or halogenide is a double salt, where one (or more) halogen atom is directly coordinated to the metal atom, such as KBBF, etc.; (2) halidoborate, halide, or halogenide is an anionic species, where one (or more) halogen atom is directly coordinated to the B atom, such as ABF_4 (A = Na, K). In this study, we are still interested in the halogen-containing borates. We try to introduce the largest-electronegativity F anion into borates. It is reported that the incorporation of an F anion can efficiently widen the transparent window of materials, making them more suitable for UV applications. Also, Albrecht-Schmitt et al.[13] state that, compared to the BO_4 tetrahedra, the partial substitution of O atoms by F atoms will further reduce the symmetry; thus, a noncentrosymmetric structure could yield a larger NLO response based on polarization of the B−F bond. Compared to oxygen anions, the F anions are more likely to be terminal instead of bridging, which favors functionalization of the structure of sheets and frameworks. Guided by these ideas, two halogen-containing borates, $Li_6RbB_2O_6F$ and $K_3B_3O_3F_6$, have been synthesized by a high-temperature solution method under ambient pressure. According to the definition described above, $Li_6RbB_2O_6F$ should be the borate fluoride, in which all of the F atoms connect with the cations rather than the B atoms, while $K_3B_3O_3F_6$ should be the fluoroborate, in which the interesting B−F bonds are observed. In the structure of $Li_6RbB_2O_6F$, the $[Li_3B_3O_6]_\infty$ layer similar to the $[Be_3B_3O_6]_\infty$ layers in $Sr_2Be_2B_2O_7$ (SBBO)[2a] and the $[RbF]_\infty$ layers similar to graphene are observed, and according to the conception of salt-inclusion compound reported by Hwu et al.,[14] $Li_6RbB_2O_6F$ can also be regarded as a salt-inclusion compound. In addition, it is worth noting that all of the reported borate fluorides seem to focus on the alkaline-earth borate, while as far as we know, there are no reports about borate fluorides that only contain alkaline-metal cations. Therefore, $Li_6RbB_2O_6F$ seems to represent the first example of alkali-metal borate fluoride. For $K_3B_3O_3F_6$, although Andriiko et al. reported the formation of $K_3B_3O_3F_6$ and depicted an orthorhombic crystal system.[15a] Subsequently, Jansen et al.

Received: October 31, 2014
Published: December 1, 2014

dx.doi.org/10.1021/ic502625b | *Inorg. Chem.* 2014, 53, 12686−12688

also referred to the molecular formula $K_3B_3O_3F_6$.[15c] However, the crystal structure of $K_3B_3O_3F_6$ still could not be obtained until now. In our current research, we synthesized $K_3B_3O_3F_6$ with a traditional solid-state reaction technique and grew a small size single crystal of $K_3B_3O_3F_6$ using a high-temperature solution method under ambient pressure for the first time. A high-temperature solution method was used to grow the fluoroborate, which is really difficult in open air, because the B−F bonds tend to be oxidized. However, our current research shows that $K_3B_3O_3F_6$ can be stable in open air and the crystal can be grown by the high-temperature solution method. Therefore, we believe that our current research will guide the syntheses and growth of other new alkine-metal borate fluorides and fluoroborates using the high-temperature solution method under ambient pressure.

$Li_6RbB_2O_6F$ crystallizes in the orthorhombic space group *Pnma*. In the structure, the B atom has only one coordinated environment to form the planar BO_3 triangle. The Li atoms with three unique positions are all in a four-coordinated environment. The Li(1) atoms are coordinated by three O atoms and one F atom to form $Li(1)O_3F$ tetrahedra, while the Li(2) and Li(3) atoms are both connected with four O atoms to form LiO_4 tetrahedra. The planar BO_3 triangles connect with the Li(1) atoms to form alveolate $[Li_3B_3O_6]_\infty$ layers (Figure 1a). The alveolate layers are linked up via F atoms to give double layers with tunnels running along the *a* axis, where the Rb atoms reside (Figure 1b). The LiO_4 tetrahedra assist in coupling the double layers together to generate the three-dimensional (3D) network.

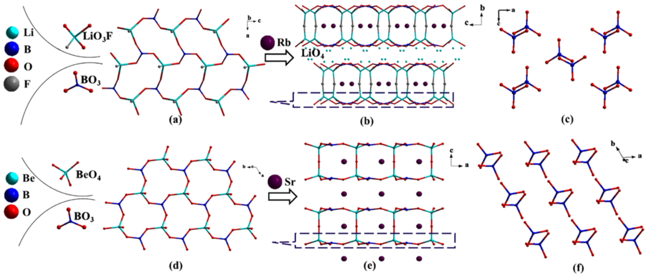

Figure 1. (a) $[Li_3B_3O_6]_\infty$ layer in $Li_6RbB_2O_6F$. (b) 3D framework of $Li_6RbB_2O_6F$ with Li (Rb)−O and Rb−F bonds omitted for clarity viewed along the *a* axis. (c) Arrangement of the BO_3 groups in $Li_6RbB_2O_6F$. (d) $[Be_3B_3O_6]_\infty$ layers in SBBO. (e) 3D framework of SBBO with Sr−O bonds omitted for clarity viewed along the *b* axis. (c) Arrangement of the BO_3 groups in SBBO.

Interestingly, the structure of $Li_6RbB_2O_6F$ is similar to that of SBBO.[2a] The $[Li_3B_3O_6]_\infty$ layers of $Li_6RbB_2O_6F$ can be treated as the $[Be_3B_3O_6]_\infty$ layers in SBBO, in which the BeO_4 tetrahedra are replaced by the LiO_3F tetrahedra. The adjacent $[Be_3B_3O_6]_\infty$ layers are bridged via O atoms, forming double layers, with the tunnel running along the *b* axis, where the Sr(1) atoms reside (Figure 1d). The $Sr(2)O_8$ polyhedra assist in coupling the double layers together by sharing O atoms to generate a 3D network (Figure 1d,e). In addition, the BO_3 triangles in the $[Li_3B_3O_6]_\infty$ layers have an arrangement similar to that of SBBO; all BO_3 triangles nearly adopt a coplanar configuration, which can favor the promotion of birefringence. The calculation result suggests that the birefringence of $Li_6RbB_2O_6F$ is about 0.06 in the visible region (Figure S1 in the SI). The other structure characters are the graphene-like $[RbF]_\infty$ layers (Figure S2 in the SI), which have also been observed in beryllium borates or other borates, just giving a few examples, beryllium borates including KBe_2BO_3F,[16a] $Na_2CsBe_6B_5O_{15}$,[16b] $MBe_2B_3O_7$ (M = Rb, K),[16c] etc., other borates including $M_2Cd_3B_{16}O_{28}$ (M = Rb, Cs),[17a] and $Na_{11}B_{21}O_{36}X_2$ (X = Cl, Br)[17b] reported by our group. The difference is that the $[RbF]_\infty$ layers in $Li_6RbB_2O_6F$ are electrically neutral, which is little observed in borate. However, the weak bond strength between the Rb and F atoms may lead to the instability of $Li_6RbB_2O_6F$ compound. Thus, during the synthesis of a pure phase of $Li_6RbB_2O_6F$, which cannot be obtained, the phase of $Li_6B_2O_6$ stably exists, and there are also some unknown phases (Figure S3 in the SI).

$K_3B_3O_3F_6$ crystallizes in the monoclinic space group $P2_1/n$. In the structure, the fundamental building block $B_3O_3F_6$ consists of three tetrahedrally coordinated B atoms, which coordinate by two O atoms and two F atoms to form BO_2F_2 tetrahedra and then are further shared by the K atoms to form a 3D network (Figure 2). The K(1) and K(2) atoms are coordinated by ten atoms to form KO_2F_8 polyhedra while K(3) atoms are coordinated by three O atoms and six F atoms. The pure phase of $K_3B_3O_3F_6$ has been characterized by the powder X-ray diffraction (XRD). The result is that the experimental XRD pattern is in agreement with the calculated one based on the single-crystal crystallographic data of $K_3B_3O_3F_6$ (Figure S4 in the SI). The B atom surrounded by three or four O atoms is a common feature in borates, while the B atom surrounded by the F atom is rarely seen. There are only a few oxygen-containing compounds including the B−F bond (e.g., $Li_2C_2O_4BF_2$,[18a] $C_2H_{10}N_2(BPO_4F_2)$,[18b] $Li_2B_6O_9F_2$,[8a] LiB_6O_9F,[8b] $Li_2B_3O_4F_3$,[8c] $Na_3B_3O_3F_6$,[15b,c] and BiB_2O_4F[19]). They are all synthesized under hydrothermal conditions or in a purified argon atmosphere using a standard Schlenk technique.[15b] Only $BaBOF_3$ including the B−F bond has been synthesized by the high-temperature solution, but in the structure, the bond distance information turns out to be very suspicious.[20] Thus, $K_3B_3O_3F_6$ appear to be the first alkali-metal fluoroborate crystal grown by the high-temperature solution method in air. These indicate that the open high-temperature solution method may also be a feasible method to grow the fluoroborate.

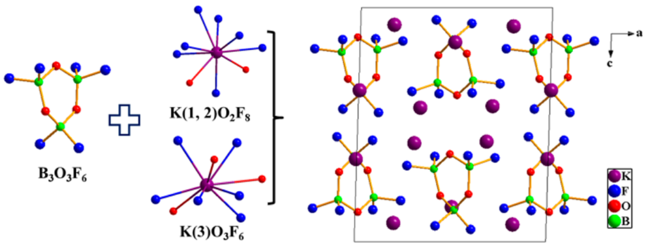

Figure 2. Structure of $K_3B_3O_3F_6$ with K−O(F) bonds omitted for clarity viewed along the *b* axis.

In the IR spectrum of $K_3B_3O_3F_6$ (Figure S5 in the SI), the strong absorption peak at 1386 cm^{-1} is ascribed for the ring stretching vibrations.[21a] The peaks at 1201, 1076, and 921 cm^{-1} are attributed to the characteristic stretching vibrations, manifesting the hexafluorotriborate ring.[21b] The peak at 783 cm^{-1} discloses the B−F stretching vibration of the BO_2F_2 groups.[21c] The peak at 561 cm^{-1} is interpreted for the ring deformation vibration. The IR spectrum further confirms the existence of the $B_3O_3F_6$ rings, consistent with the results obtained from the single-crystal X-ray structural analyses. To gain insight into the nature of the chemical bonding of $K_3B_3O_3F_6$, the band structures and densities of states (DOS) were calculated based on density functional theory.[22] It is worth noting that, from the deformation charge-density map (Figure S6 in the SI), strong covalent B−F(O) bonds have been found. In addition, $K_3B_3O_3F_6$ is a direct energy gap with a band gap of 5.96 eV, which is similar to the experimental one of 6.1 eV derived from the UV−vis−IR diffuse-reflection spectrum (Figures S7 and S8 in the SI). The fundamental optical transition is believed to originate from the filled O 2p and F 2p states in the valence band to the empty K 3s and 3p states and small amounts of B 2p states in the conduction band based on the total and partial DOS. The thermal behavior suggests that $K_3B_3O_3F_6$ melts at 432 °C, along with the volatilization (Figure S9 in the SI).

■ CONCLUSIONS

Two novel halogen-containing borates have been prepared by a high-temperature solution method. $Li_6RbB_2O_6F$ appears to be the first borate fluoride in alkali-metal borates. Also, the favorable structure features of SBBO are maintained in the structure of $Li_6RbB_2O_6F$; namely, the nearly planar $[Li_3B_3O_6]_\infty$ layers with all BO_3 groups retain a coplanar configuration for producing large birefringence. However, in the structure of $K_3B_3O_3F_6$, the unique linkage mode of the B atoms directly connecting the F atoms has been observed. $K_3B_3O_3F_6$ appears to be the first fluoroborate synthesized by an open high-temperature solution method. That provides the new synthesis strategy to obtain the fluoroborate under ambient pressure.

■ ASSOCIATED CONTENT

Supporting Information

Experimental details, crystallographic information files in CIF format, selected bond lengths and angles, and figures of powder XRD and crystal structures. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: slpan@ms.xjb.ac.cn.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work is supported by the “Western Light Foundation” Program of CAS (Grant XBBS201214), the 973 Program of China (Grant 2014CB648400), the National Natural Science Foundation of China (Grants U1303392 and 21201176), and the Xinjiang Program of Cultivation of Young Innovative Technical Talents (Grant 2014711001).

■ REFERENCES

(1) (a) Becker, P. *Adv. Mater.* **1998**, *10*, 979−992. (b) Chen, C. T.; Wu, B. C.; Jiang, A.; You, G. *Sci. Sin., Ser. B (Engl. Ed.)* **1985**, *28*, 235−243.

(2) (a) Chen, C. T.; Wang, Y. B.; Wu, B. C.; Wu, K. C.; Zeng, W. L.; Yu, L. H. *Nature* **1995**, *373*, 322−324. (b) Ok, K. M.; Halasyamani, P. S. *Chem. Soc. Rev.* **2006**, *35*, 710−717. (c) Wang, S. C.; Ye, N.; Zou, G. H. *Inorg. Chem.* **2014**, *53*, 2742−2748. (d) Wang, S. C.; Ye, N.; Zou, G. H. *CrystEngComm* **2014**, *16*, 3971−3976.

(3) (a) Marvel, M. R.; Lesage, J.; Baek, J.; Halasyamani, P. S.; Stern, C. L.; Poeppelmeier, K. R. *J. Am. Chem. Soc.* **2007**, *129*, 13963−13969. (b) Donakowski, M. D.; Gautier, R.; Lu, H. C.; Thao Tran, T.; Cantwell, J. R.; Halasyamani, P. S.; Poeppelmeier, K. R. *Inorg. Chem.* **2014**, DOI: 10.1021/ic501486x.

(4) (a) Bader, R. F. W. *Mol. Phys.* **1960**, *3*, 137−140. (b) Bader, R. F. W. *Can. J. Chem.* **1962**, *40*, 1164−1175. (c) Pearson, R. G. *J. Am. Chem. Soc.* **1969**, *91*, 4947−4955.

(5) (a) Ra, H. S.; Ok, K. M.; Halasyamani, P. S. *J. Am. Chem. Soc.* **2003**, *125*, 7764−7769. (b) Yeon, J.; Kim, S.; Nguyen, S. D.; Lee, H.; Halasyamani, P. S. *Inorg. Chem.* **2012**, *51*, 2662−2668.

(6) (a) Rong, C.; Yu, Z. W.; Wang, Q.; Zheng, S. T.; Pan, C. Y.; Deng, F.; Yang, G. Y. *Inorg. Chem.* **2009**, *48*, 3650−3659. (b) Cheng, L.; Wei, Q.; Wu, H. Q.; Zhou, L. J.; Yang, G. Y. *Chem.—Eur. J.* **2013**, *19*, 17662−17667.

(7) (a) Zhang, J. H.; Hu, C. L.; Xu, X.; Kong, F.; Mao, J. G. *Inorg. Chem.* **2011**, *50*, 1973−1782. (b) Hao, Y. C.; Hu, C. L.; Xu, X.; Kong, F.; Mao, J. G. *Inorg. Chem.* **2013**, *52*, 13644−13650.

(8) (a) Pilz, T.; Jansen, M. *Z. Anorg. Allg. Chem.* **2011**, *637*, 1−6. (b) Cakmak, G.; Nuss, J.; Jansen, M. *Z. Anorg. Allg. Chem.* **2009**, *635*, 631−636. (c) Pilz, T.; Nuss, H.; Jansen, M. *J. Solid State Chem.* **2012**, *186*, 104−108.

(9) (a) Chen, C. T.; Wang, Y. B.; Xia, Y. N.; Wu, B. C.; Tang, D. Y.; Wu, K. C.; Zeng, W. R.; Yu, L. H.; Mei, L. F. *J. Appl. Phys.* **1995**, *7*, 2268−2272. (b) Huang, H. W.; Yao, J. Y.; Lin, Z. H.; Wang, X. Y.; He, R.; Yao, W. J.; Zhai, N. X.; Chen, C. T. *Chem. Mater.* **2011**, *23*, 5457−5463.

(10) (a) Wu, H. P.; Pan, S. L.; Poeppelmeier, K. R.; Li, H. Y.; Jia, D. Z.; Chen, Z. H.; Fan, X. Y.; Yang, Y.; Rondinelli, J. M.; Luo, H. S. *J. Am. Chem. Soc.* **2011**, *133*, 7786−7790. (b) Wu, H. P.; Yu, H. W.; Yang, Z. H.; Hou, X. L.; Su, X.; Pan, S. L.; Poeppelmeier, K. R.; Rondinelli, J. M. *J. Am. Chem. Soc.* **2013**, *135*, 4215−4218.

(11) (a) Yu, H. W.; Wu, H. P.; Pan, S. L.; Yang, Z. H.; Su, X.; Zhang, F. F. *J. Mater. Chem.* **2012**, *22*, 9665−9670. (b) Huang, Z. J.; Su, X.; Pan, S. L.; Dong, X. Y.; Han, S. J.; Yu, H. W.; Dong, L. Y.; Zhang, M.; Yang, Z. H. *Scr. Mater.* **2013**, *69*, 449−453. (c) Li, H. Y.; Wu, H. P.; Su, X.; Yu, H. W.; Pan, S. L.; Yang, Z. H.; Lu, Y.; Han, J.; Poeppelmeier, K. R. *J. Mater. Chem. C* **2014**, *2*, 21704−21709.

(12) Yu, H. W.; Wu, H. P.; Pan, S. L.; Wang, Y.; Yang, Z. H.; Su, X. *Inorg. Chem.* **2013**, *52*, 5359−5365.

(13) Wang, S.; Alekseev, E. V.; Diwu, J.; Miller, H. M.; Oliver, A. G.; Liu, G. K.; Depmeier, W.; Albrecht-Schmitt, T. E. *Chem. Mater.* **2011**, *23*, 2931−2939.

(14) (a) West, J. P.; Hwu, S. J. *J. Solid State Chem.* **2012**, *195*, 101−108. (b) Mo, X.; Hwu, S. J. *Inorg. Chem.* **2003**, *42*, 3978−3982.

(15) (a) Andriiko, A. A.; Parkhomenko, N. I.; Antishko, A. N. *Russ. J. Inorg. Chem.* **1988**, *33*, 410−415. (b) Güliz Cakmak, V. V. *Synthesis and Characterization of Ion Conducting Solid Polyelectrolytes and Alkali Fluorooxoborates*; Max-Planck-Institut fur Festkorperforschung: Stuttgart, Germany, 2009. (c) Cakmak, G.; Pilz, T.; Jansen, M. *Z. Anorg. Allg. Chem.* **2012**, *638*, 1411−1415.

(16) (a) Lin, Z. S.; Wang, Z. Z.; Chen, C. T.; Chen, S. K.; Lee, M. H. *Chem. Phys. Lett.* **2003**, *367*, 523−527. (b) Wang, S. C.; Ye, N.; Li, W.; Zhao, D. *J. Am. Chem. Soc.* **2010**, *132*, 8779−8785. (c) Wang, S. C.; Ye, N. *J. Am. Chem. Soc.* **2011**, *133*, 11458−11453.

(17) (a) Dong, X. Y.; Shi, Y. J.; Zhou, Z. X.; Pan, S. L.; Yang, Z. H.; Zhang, B. B.; Yang, Y.; Chen, Z. H.; Huang, Z. J. *Eur. J. Inorg. Chem.* **2013**, *2013*, 203−207. (b) Dong, X. Y.; Wu, H. P.; Shi, Y. J.; Yu, H. W.; Yang, Z. H.; Zhang, B. B.; Chen, Z. H.; Yang, Y.; Huang, Z. J.; Pan, S. L.; Zhou, Z. X. *Chem.—Eur. J.* **2013**, *19*, 7338−7342.

(18) (a) Zhang, S. S. *Electrochem. Commun.* **2006**, *8*, 1423−1425. (b) Huang, Y. X.; Schäfer, G.; Borrmann, H.; Zhao, J. T.; Kniep, R. *Z. Anorg. Allg. Chem.* **2003**, *629*, 3−7.

(19) Cong, R. H.; Sun, J. L.; Yang, T.; Li, M. R.; Liao, F. H.; Wang, Y. X.; Lin, J. H. *Inorg. Chem.* **2011**, *50*, 5098−5103.

(20) Chackraburtty, D. M. *Acta Crystallogr.* **1957**, *10*, 199−200.

(21) (a) Fischer, H. D.; Lehmann, W. J.; Shapiro, I. *J. Phys. Chem.* **1961**, *65*, 1166−1168. (b) Maya, L. *J. Am. Ceram. Soc.* **1977**, *60*, 323−326. (c) Von Barner, J. H.; Andersen, K. B.; Berg, R. W. *J. Mol. Liq.* **1999**, *83*, 141−151.

(22) Delley, B. *J. Chem. Phys.* **2000**, *113*, 7756−7764.