View Article Online

ChemComm

Chemical Communications

Accepted Manuscript

This article can be cited before page numbers have been issued, to do this please use: Y. Liu, H. Peng and W. Liao, *Chem. Commun.*, 2020, DOI: 10.1039/D0CC07443H.



This is an Accepted Manuscript, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this Accepted Manuscript with the edited and formatted Advance Article as soon as it is available.

You can find more information about Accepted Manuscripts in the Information for Authors.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard <u>Terms & Conditions</u> and the <u>Ethical guidelines</u> still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this Accepted Manuscript or any consequences arising from the use of any information it contains.



rsc.li/chemcomm

Journal Name



A Lead-Free Bismuth Iodide Organic-Inorganic Ferroelectric Semiconductor

Yu-Hua Liu,[†] Hang Peng[†] and Wei-Qiang Liao^{*}

Received 00th January 20xx, Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

Published on 11 December 2020. Downloaded by Auckland University of Technology on 12/15/2020 8:08:19 PM

Organic-inorganic metal halide ferroelectric semiconductors are mainly the lead halide ones, suffering from the toxic lead. Herein, we report a lead-free bismuth iodide ferroelectric semiconductor [1,4-butanediammonium]Bil₅, showing a high Curie temperature of 365 K and a small band gap of 1.95 eV, smaller than those of most lead halide counterparts.

Ferroelectrics, which simultaneously possess ferroelectricity, pyroelectricity, and piezoelectricity, is a kind of important functional materials with wide technical applications such as in non-volatile memory, infrared detector, piezoelectric sensors and second-order nonlinear switches.1 Ferroelectrics are generally insulators.²⁻⁵ The integration of semiconducting property into ferroelectrics has gained great interest since it obtains ferroelectric semiconductors for promising optoelectronic applications.⁶⁻¹⁰ Ferroelectric semiconductors have been found to show fascinating optoelectronic features such as the electric field controllable photoelectric response, the polarization-dependent photovoltaic effect, and the ultrafast shift current, and the spontaneous polarization in ferroelectric semiconductors is able to generate a built-in electric field for promoting the separation of photoexcited carriers.⁶⁻⁹ However, although some inorganic ferroelectric semiconductors like BiFeO3, SbSI, and GeTe have been documented,⁷⁻⁹ ferroelectric semiconductors are rare compared to the abundant ferroelectric family.²

Organic-inorganic metal halides (OIMHs) combine the advantages of both the organic and inorganic components,¹¹⁻¹⁵ providing rich opportunities for constructing multifunctional ferroelectrics.¹⁶⁻¹⁹ Their crystal structures are typically composed of inorganic metal halide frameworks separated by organic cations, where the dynamic change of organic cation is

easy to be triggered to induce ferroelectric phase transition, while the diversity of inorganic building blocks offers various functional properties such as magnetism, thermochromism, and photoluminescence.¹⁶⁻²⁰ OIMHs also feature mechanical flexibility, easy processing, light weight, and low cost.11-20 Inspired by the development of organic-inorganic lead halides as promising semiconductors for photovoltaic applications because of their excellent semiconducting properties,²¹ much attentions have been paid on lead halide OIMHs for searching for ferroelectric semiconductors in recent years.²²⁻³¹ As a result, numbers of lead halide organic-inorganic ferroelectric semiconductors have been constructed,²²⁻³¹ such as the lead chloride (C₇H₁₀N)₂PbCl₄,²² lead bromide (C₆H₁₄N)₂PbBr₄,²³ and lead iodide (C₅H₁₀F₂N)₂PbI₄.²⁴ Some of them present intriguing optoelectronic properties for next-generation optoelectronic applications.25-29 For example, polarization-induced ferroelectric photovoltaic effect and polarization-sensitive photodetection was found in ferroelectric semiconductors (C₆H₁₂F₂N)₂PbI₄ and (C₄H₁₂N)₂(CH₃NH₃)Pb₂Br₇, respectively.^{25,26} Nevertheless, the highly toxic Pb in the lead halide OIMHs is an impediment for their future applications. In view of this, it is very desirable for developing lead-free organic-inorganic ferroelectric semiconductors.

Due to the compositional multiplicity of OIMHs, the Pb(II) can be replaced by other alternatives like Sn(II), Ge(II), Sb(III) and Bi(III) to maintain the semiconducting property in OIMHs.³²⁻³⁴ Among them, the Bi(III) cation has the same $6s^26p^0$ electronic configuration as Pb(II) cation and has good air and humidity stability.³⁴ The bismuth iodide OIMHs with strong photoabsorption represented by [CH₃NH₃]₃Bi₂I₉ have shown the potential as photovoltaic materials,^{32,34} while most of them exhibit no clear ferroelectricity, although their crystal structures have been well studied.³⁵⁻⁴⁰ To our knowledge, there are only two bismuth iodide hybrid ferroelectrics [NH₃(CH₃)₆NH₃]BiI₅³⁹ and [NH₂CHNH₂]₃Bi₂I₉.⁴⁰ Discovering a new bismuth iodide hybrid ferroelectric remains a great challenge because of the lack of in-depth knowledge on the relationship between ferroelectricity and crystal structure. Herein, we reported a new

College of Chemistry, Nanchang University, Nanchang 330031, People's Republic of China. E-mail: liaowq@ncu.edu.cn

Electronic Supplementary Information (ESI) available: The experimental details and characterization. CCDC 2036251-2036252. For ESI and crystallographic date in CIF or other electronic format see DOI: 10.1039/x0xx00000x +These authors contributed equally to this work.

Published on 11 December 2020. Downloaded by Auckland University of Technology on 12/15/2020 8:08:19 PM

Journal Name

lead-free bismuth iodide organic-inorganic ferroelectric semiconductor [1,4-butanediammonium]Bil₅ ([NH₃(CH₂)₄NH₃]Bil₅, 1), which shows clear ferroelectricity with saturation polarization of 1.35 μ C/cm² and a small band gap of 1.95 eV. [1,4-butanediammonium]Bil₅ undergoes a hightemperature ferroelectric-to-paraelectric phase transition with the Curie temperature (T_c) as high as 365 K, significantly higher than that (203 K) of $[NH_2CHNH_2]_3Bi_2I_9^{39}$ and is comparable to that (379 K) of $[NH_3(CH_3)_6NH_3]BiI_5$.⁴⁰ It is worth emphasizing that the band gap of 1.95 eV of [1,4-butanediammonium]BiI $_{\rm 5}$ is smaller than the 2.7 eV of typical inorganic ferroelectric semiconductor $BiFeO_3$ and those (above 2.2 eV) of most lead halide organic-inorganic ferroelectric semiconductors.22-31 These findings throw light on the exploration of more lead-free organic-inorganic metal halide ferroelectric semiconductors toward future device applications.



Fig. 1 Packing views of the crystal structure of **1** at (a) 293 K in the FP and (b) 383 K in the PP. Hydrogen atoms were omitted for clarity. The dash line denotes the mirror plane perpendicular to the *b* axis.



Fig. 2 (a) DSC curves of **1**. (b) SHG intensity of **1** as a function of temperature. (c) temperature-dependent ε' of **1**. (d) *P*–*E* hysteresis loop of **1** obtained at 345 K.

We obtained compound ${\bf 1}$ as dark-red crystals by slow evaporation of an aqueous HI solution containing equimolar amounts of [1,4-butanediammonium]I_2 and BiI_3. The phase

purity of as-grow crystals was verified by powdercle X riay diffraction results (Fig. S1). The crystal structure 30 10 was then determined by single-crystal X-ray diffraction measurements. At 293 K, 1 crystallizes in the monoclinic crystal system with the polar space group $P2_1$ and the point group 2 (Table S1). The polar $P2_1$ phase is the ferroelectric phase (FP) of **1**. The basic structure consists of one-dimensional zigzag [Bil₅]_n²⁻ chains and types of crystallographically dependent three 1.4butanediammonium cations (Fig. 1a). The $[Bil_5]_n^{2-}$ chain is formed by corner-sharing Bil₆ octahedra and shows the cisconformation. Due to the electron lone pair effect of 6s² in the Bi(III) cation,⁴¹ the Bil₆ octahedron shows a severe distortion, as revealed by the Bi-I bond distances (2.9142(12)-3.2842(11) Å) and I-Bi-I angles (82.26(3)°- 100.20(3)° for cis-I-Bi-I angles, 169.12(4)°-176.81(3)° for trans-I-Bi-I angles) (Table S2). The 1,4-butanediammonium cations reside in the free spaces between adjacent $[Bil_5]_n^{2-}$ chains. All the three kinds of 1,4butanediammonium cations display an ordered state since they occupy general symmetry positions. As Fig. 1a shows, the ammonium heads of 1,4-butanediammonium cations orient along the b axis. This should arouse the polarization along the b axis, which is the polar axis of the $P2_1$ ferroelectric phase. The 1,4-butanediammonium cations connect with the $[BiI_5]_n^{2-}$ chains through N–H···I hydrogen-bonding interactions with the average N…I distance being of 3.683 Å (Fig. S2).

The crystal structure of 1 at 383 K adopts a different space group of centrosymmetric monoclinic $P2_1/m$ with the point group of 2/m (Table S1). The centrosymmetric $P2_1/m$ phase corresponds to the paraelectric phase (PP) of **1**. In PP, the Bil₆ octahedron remains distorted with Bi-I bond distances of 2.9381(15)-3.282(3) Å, cis-I-Bi-I angles of 81.90(4)-100.33(6)° and trans-I-Bi-I angles of 166.14(6)-177.92(6)° (Table S2), which show minor differences from those in FP. The Bi-I-Bi angles change more obviously from FP (160.57(4)-174.93(6)°) to (166.02(10)-180.00(3)°). This indicates the minor PP deformation of the anionic $[Bil_5]_n^{2-}$ chains. There are also three kinds of crystallographically non-equivalent 1,4butanediammonium cations in PP, but they lie on a special symmetry position of the mirror plane perpendicular to the b axis and show two-fold orientational disorder over two equivalent positions (Fig. 1b). The dipole moments of 1,4butanediammonium cations offset each other along the *b* axis. The FP-to-PP phase transition of **1** thus originates from the main contribution of order-disorder transition of 1,4butanediammonium cations and the minor contribution of deformation of the anionic $[BiI_5]_n^{2-}$ chains.

We then detected the FP-to-PP phase transition of **1** by DSC (differential scanning calorimetry) measurements. The DSC curves of **1** show a pair of small heat anomalies at 365/363 K in the heating/cooling run (Fig. 2a), demonstrating that the phase transition occurs reversibly at T_c of 365 K and is of second-order type. We obtained the entropy change (ΔS) as 2.91 J/(mol·K). From the Boltzmann equation, $\Delta S = R \ln(N)$, where R and N is the gas constant and the ratio of the number of respective geometrically distinguishable orientations, respectively, the N value is calculated as 1.42, which shows the order-disorder feature of the phase transition. We also carried out the

Published on 11 December 2020. Downloaded by Auckland University of Technology on 12/15/2020 8:08:19 PM

Journal Name

COMMUNICATION

experiments of temperature-dependent SHG (second harmonic generation) response of 1 to confirm the crystal symmetry change accompanying the phase transition. As Fig. 2b shows, 1 displays non-zero SHG intensity below T_c in FP, coinciding with the noncentrosymmetric polar P21 crystal symmetry. Upon heating, the SHG intensity gradually weakens in FP and reaches almost zero near and above T_{c_r} which is consistent with the noncentrosymmetric P2₁/m crystal symmetry in PP. Thermogravimetric analysis of 1 reveals its thermal stability reaching 620 K (Fig. S3), far higher than the T_c . The T_c (365 K) of **1** is a high one among molecular ferroelectrics,^{2,3} and is higher than those of the lead halide OIMH ferroelectrics (C₅H₁₄N)₂(CH₃NH₃)₂Pb₃Br₁₀ (305 K),²⁹ (C₄H₁₁IN)PbI₃ (312 K),³⁰ and the bismuth iodide [NH₂CHNH₂]₃Bi₂I₉ (203 K).⁴⁰

We further investigated the FP-to-PP phase transition of 1 by dielectric measurements. The dielectric real part (ϵ ') values of the single-crystal sample of 1 at frequencies of 1000-1 kHz along the polar b axis show giant λ -shape peaks at around T_c with the peak ε' value up to 1100–1700, which is about a hundred times of the ε' value in the peak valley (Fig. 2c). This further confirms the FP-to-PP nature of the phase transition at $T_{\rm c}$. The peak temperature displays no shift from 1000 kHz to 1 kHz, which indicates that there is no critical slowing down of the relaxation time. The tan δ shows obvious dielectric anomaly at around T_c as well (Fig. S4). We measured the P-E (polarization-electric field) hysteresis loops of 1 to directly detect its ferroelectricity. The single-crystal sample of 1 along the polar b axis shows a good P-E hysteresis loop at 345 K in FP (Fig. 2d), which clearly proves the ferroelectricity of 1. We obtained the P_s (saturation polarization) of 1.35 μ C/cm², significantly larger than the 0.02 μ C/cm² of [NH₂CHNH₂]₃Bi₂I₉ and has the same magnitude as the 6.2 μ C/cm² of [NH₃(CH₃)₆NH₃]Bil₅.^{39,40}

PFM (Piezoresponse force microscopy) has significant merits in mapping and/or manipulating the ferroelectric domains.²⁴ We polished the (010) plane of the prepared single-crystal sample of **1**. The polarization direction is perpendicular to the (010) plane. The vertical PFM images (Fig. 3b and c) show the presence of irregular shaped ferroelectric domains. Domain walls appear as dark lines in the amplitude image, and the PFM phase signal inverts by ~180° between adjacent domains in the corresponding phase image, indicating the polarization points upward or downward. It is note that the PFM mapping shows that the domain pattern has no crosstalk with the surface morphology, excluding any rough surface induced ambiguities during the PFM measurements.

To confirm switching of the polarization in **1**, we performed the switching spectroscopy PFM (SS-PFM) measurements firstly on (010)-oriented crystal, which provides microscopic knowledge about the switching dynamics, such as the threshold voltage.^{24,25} The out-of-plane piezoresponse acquired as a function of DC voltage exhibited clear hysteresis in both amplitude (Fig. 4h) and phase (Fig. 4i) loops. At the voltages of about ±30 V, a sharp phase shift by 180° and accompanying amplitude minimum were clearly observed, corresponding to the threshold voltage, demonstrating switching between the upward and downward polarization states. Larger region of domain switching in the (010)-oriented crystal is realized via the electrical writing, reconfirming the ferroelectricity 06F 01.44Åh initial downward polarization state was selected (Fig. 4a and b). Domain switching was performed by scanning the dashed black box area with PFM tip under a bias of -50 V. The followed PFM imaging shows the resulting domain pattern: the central area has been polarized upward (Fig. 4c and d). Next, the newly poled region can be switched back simply by application of a positive voltage of +40 V (Fig. 4e and f). Fig. 4g shows the surface morphology of the scanned region after two steps of electrical writing, showing no damage after the electric writing.



Fig. 3 Vertical PFM mapping on the (010)-oriented single-crystal surface of **1**. (a) Topographic, (b) PFM amplitude and (c) PFM phase images.



Fig. 4 Vertical PFM images (left column: amplitude; middle column: phase) of electrical written domains in the (010)-oriented single crystal of **1**. (a, b) An initial state with downward polarization. (c, d) The same area after scanning the black boxed area with voltage of -50 V. (e, f) After scanning the smaller boxed region with voltage of +40 V. (g) Topography image after two steps of electric writing. Scale bar, 5 μ m. (h, i) PFM phase (h) and amplitude (i) response as a function of applied DC voltage.

Organic-inorganic bismuth iodides are typical semiconductors.32,34 We recorded the UV-vis (ultraviolet-visible) absorption spectra of 1 to determine its band gap. As Fig. 5 shows, 1 exhibits a strong absorption at around 650 nm, being in accordance with the dark-red color appearance of 1. The variation trend of absorption coefficient as a function of photo energy shows the feature of indirect band gap semiconductor, as found in other organic-inorganic bismuth iodides.³⁹ The band gap of **1** is obtained as 1.95 eV from the *Tauc* plot, which is comparable to the $[NH_3(CH_3)_6NH_3]Bil_5$ (1.89) eV) since the band gaps of organic-inorganic bismuth iodides are mainly determined by the inorganic bismuth iodide framework.³⁹ It is worth noting that the band gap of **1** is smaller than those of most lead halide organic-inorganic ferroelectric

Ceptec

semiconductors (above 2.2 eV)²²⁻³¹ and the lead-free photovoltaic absorber $[CH_3NH_3]Bi_2I_9$ (2.1 eV),³² showing the potential as lead-free photovoltaic materials.



Fig. 5 UV-vis absorption spectrum of 1. Inset: the Tauc plot.

In summary, we demonstrated a new lead-free organicinorganic ferroelectric semiconductor [1,4butanediammonium]Bil₅, which undergoes a FP-to-PP phase transition at 365 K. It shows a saturation polarization of 1.35 μ C/cm² and displays a small band gap of 1.95 eV, which is outstanding in ferroelectric semiconductors. This work enriches the family of lead-free metal halide ferroelectric semiconductor and should shed light on the exploration of more superior ones.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (91856114 and 21703033).

Conflicts of interest

There are no conflicts to declare.

Notes and references

- M. E. Lines and A. M. Glass, Principles and applications of ferroelectrics and related materials, Oxford University Press, 2001.
- 2 W. Zhang and R.-G. Xiong, Chem. Rev., 2012, 112, 1163.
- 3 P.-P. Shi, Y.-Y. Tang, P.-F. Li, W.-Q. Liao, Z.-X. Wang, Q. Ye and R.-G. Xiong, *Chem. Soc. Rev.*, 2016, **45**, 3811.
- 4 Y. Ai, D. J. Wu, M. J. Yang, P. Wang, W. H. He and W. Q. Liao, *Chem. Commun.*, 2020, 56, 7033.
- 5 H. Y. Zhang, Si. Q. Lu, X. Chen, R. G. Xiong and Y. Y. Tang, *Chem. Commun.*, 2019, **55**, 11571.
- 6 Y. B. Yuan, Z. G. Xiao, B. Yang and J. S. Huang, J. Mater. Chem. A, 2014, 2, 6027.
- 7 T. Choi, S. Lee, Y. J. Choi, V. Kiryukhin and S.-W. Cheong, *Science*, 2009, **324**, 63.
- 8 S.-J. Gong, F. Zheng and A. M. Rappe, *Phys. Rev. Lett.*, 2018, 121, 017402.
- 9 M. Sotome, M. Nakamura, J. Fujioka, M. Ogino, Y. Kaneko, T. Morimoto, Y. Zhang, M. Kawasaki, N. Nagaosa, Y. Tokura and N. Ogawa, *Proc. Natl. Acad. Sci. U. S. A.*, 2019, **116**, 1929.
- 10 N. M. Casellas, I. Urbanaviciute, T. D. Cornelissen, J. A. Berrocal, T. Torres, M. Kemerink and M. G. Iglesias, *Chem. Commun.*, 2019, 55, 8828.
- 11 B. Saparov and D. B. Mitzi, Chem. Rev., 2016, 116, 4558-4596.
- 12 W. Li, Z. Wang, F. Deschler, S. Gao, R. H. Friend and A. K. Cheetham, *Nat. Rev. Mater.*, 2017, **2**, 16099.

- J. Zhang, S. G. Han, X. T. Liu, Z. Y. Wu, C. M. Ji, Z. H. Sun and H. Luo, Chem. Commun., 2018, 54, 56 20: 10.1039/DOCC07443H
- 14 R. G. Qiu, X. X. Chen, R. K. Huang, D. D. Zhou, W. J. Xu, W. X. Zhang and X. M . Chen, *Chem. Commun.*, 2020, **56**, 5488.
- 15 W. W. Wu, S. G. Wu, Y. C. Chen, G. Z. Huang, B. H. Lyu, Z. P. Ni and M. L. Tong, *Chem. Commun.*, 2020, **56**, 4551.
- 16 Y. Zhang, W.-Q. Liao, D.-W. Fu, H.-Y. Ye, C.-M. Liu, Z.-N. Chen and R.-G. Xiong, *Adv. Mater.*, 2015, **27**, 3942.
- 17 C. Jiang, N. Zhong, C. Luo, H. Lin, Y. Zhang, H. Peng and C.-G. Duan, *Chem. Commun.*, 2017, 53, 5954.
- C. Shi, L. Ye, Z.-X. Gong, J.-J. Ma, Q.-W. Wang, J.-Y. Jiang, M.-M. Hua, C.-F. Wang, H. Yu, Y. Zhang and H.-Y. Ye, *J. Am. Chem. Soc.*, 2020, **142**, 545.
- 19 J.-C. Liu, W.-Q. Liao, P.-F. Li, Y.-Y. Tang, X.-G. Chen, X.-J. Song, H.-Y. Zhang, Y. Zhang, Y.-M. You and R.-G. Xiong, *Angew. Chem. Int. Ed.*, 2020, **59**, 3495.
- 20 B. Huang, L.-Y. Sun, S.-S. Wang, J.-Y. Zhang, C.-M. Ji, J.-H. Luo, W.-X. Zhang and X.-M. Chen, *Chem. Commun.*, 2017, **53**, 5764.
- 21 A. K. Jena, A. Kulkarni and T. Miyasaka, Chem. Rev., 2019, 119, 3036.
- 22 W. Q. Liao, Y. Zhang, C. L. Hu, J. G. Mao, H. Y. Ye, P. F. Li, S. D. Huang and R. G. Xiong, *Nat. Commun.*, 2015, 6, 7338.
- H. Y. Ye, W. Q. Liao, C. L. Hu, Y. Zhang, Y. M. You, J. G. Mao, P. F. Li and R. G. Xiong, *Adv. Mater.*, 2016, 28, 2579-2586.
- 24 H. Y. Zhang, X. J. Song, X. G. Chen, Z. X. Zhang, Y. M. You, Y. Y. Tang and R. G. Xiong, J. Am. Chem. Soc., 2020, 142, 4925.
- 25 T. T. Sha, Y. A. Xiong, Q. Pan, X. G. Chen, X. J. Song, J. Yao, S. R. Miao, Z. Y. Jing, Z. J. Feng, Y. M. You and R. G. Xiong, *Adv. Mater.*, 2019, **31**, 1901843.
- 26 L. N. Li, X. T. Liu, Y. B. Li, Z. Y. Xu, Z. Y. Wu, S. G. Han, K. W. Tao, M. C. Hong, J. H. Luo and Z. H. Sun, *J. Am. Chem. Soc.*, 2019, 141, 2623.
- Y. Hu, F. Florio, Z. Chen, W. A. Phelan, M. A. Siegler, Z. Zhou, Y. Guo, R. Hawks, J. Jiang, J. Feng, L. Zhang, B. Wang, Y. Wang, D. Gall, E. F. Palermo, Z. Lu, X. Sun, T.-M. Lu, H. Zhou, Y. Ren, E. Wertz, R. Sundararaman and J. Shi, *Sci. Adv.*, 2020, 6, eaay4213
- 28 I. H. Park, Q. N. Zhang, K. C. Kwon, Z. Y. Zhu, W. Yu, K. Leng, D. Giovanni, H. S. Choi, I. Abdelwahab, Q. H. Xu, T. C. Sum and K. P. Loh, *J. Am. Chem. Soc.*, 2019, **141**, 15972.
- 29 M. Li, Y. Xu, S. Han, J. Xu, Z. Xie, Y. Liu, Z. Xu, M. Hong, J. Luo and Z. Sun, *Adv. Mater.*, 2020, **32**, 2002972.
- 30 X. N. Hua, W. Q. Liao, Y. Y. Tang, P. F. Li, P. P. Shi, D. Zhao and R. G. Xiong, J. Am. Chem. Soc., 2018, **140**, 12296.
- 31 C. Ji, S. Wang, L. Li, Z. Sun, M. Hong and J. Luo, Adv. Funct. Mater., 2018, 29, 1805038.
- 32 Z. Shi, J. Guo, Y. H. Chen, Q. Li, Y. Pan, H. Zhang, Y. Xia, and W. Huang, *Adv. Mater.*, 2017, **29**, 1605005.
- 33 X. Y. Wang, K. Li, H. L. Xu, N. Ali, Y.Wang, Q. B. Shen and H. Z. Wu, Chem. Commun., 2020, 56, 7917.
- 34 M. Lyu, J.-H. Yun, M. Cai, Y. Jiao, P. V. Bernhardt, M. Zhang, Q. Wang, A. Du, H. Wang and G. Liu, *Nano Res.*, 2016, 9, 692.
- 35 K. Eckhardt, V. Bon, J. Getzschmann, J. Grothe, F. M. Wisser and S. Kaskel, *Chem. Commun.*, 2016, **52**, 3058.
- 36 L. M. Wu, X. T. Wu and L. Chen, Coord. Chem. Rev., 2009, 253, 2787.
- 37 S. A. Adonin, M. N. Sokolov and V. P. Fedin, *Coord. Chem. Rev.*, 2016, **312**, 1.
- 38 N. Dehnhardt, J. N. Luy, M. Szabo, M. Wende, R. Tonner and J. Heine, *Chem. Commun.*, 2019, **55**, 14725.
- H. Y. Zhang, Z. H. Wei, P. F. Li, Y. Y. Tang, W. Q. Liao, H. Y. Ye,
 H. Cai and R. G. Xiong, *Angew. Chem. Int. Ed.*, 2018, **57**, 526.
- 40 P. Szklarz, A. Gągor, R. Jakubas, P. Zieliński, A. Piecha-Bisiorek, J. Cichos, M. Karbowiak, G. Bator and A. Ciżman, *J. Mater. Chem. C*, 2019, **7**, 3003.
- 41 R. Jakubas, M. Rok, K. Mencel, G. Bator and A. Piecha-Bisiorek, Inorg. Chem. Front., 2020, 7, 2107.

Published on 11 December 2020. Downloaded by Auckland University of Technology on 12/15/2020 8:08:19 PM.



[1,4-butanediammonium]BiI₅ is a lead-free organic-inorganic ferroelectric semiconductor showing a high Curie temperature and a small band gap.