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Thermal conductivity of a perovskite-type metal–organic framework crystal†

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We report for the first time the investigation of thermal conductivity for a perovskite-type MOF crystal. *In situ* single crystal X-ray diffraction technology was employed to track the phase transition of a newly synthesized perovskite MOF. The perovskite MOF crystal exhibits a low thermal conductivity of 1.3 W (K m)^{−1} in comparison to most of the bulk crystal materials at room temperature.

Thermoelectric materials have gained increasing attention because of their broad prospect in the field of waste-heat power generation.^{1–3} For a high-performance thermoelectric material, low thermal conductivity is one of the essential factors,⁴ while low thermal conductivity materials still remain largely unexplored. Hybrid perovskite materials, which have gained increasing attention due to their great promise in photovoltaic applications,^{5–9} exhibit inspiring low thermal conductivity.^{10,11} The simplicity of single crystal synthesis and device architecture makes the hybrid perovskite materials suitable for thermal conductivity research.^{12,13} However, the poor thermal stability and low porosity of hybrid perovskite materials largely limit their applications in various fields, such as chemical sensing fields.

As crystalline porous materials, metal–organic frameworks (MOFs) show broad applications in the fields of gas storage, gas separation, catalysis, and chemical sensing.^{14–17} Among the numerous MOF materials, perovskite-type MOFs show interesting luminescence, ferroelectric, magnetic, and multi-ferroic properties due to their perovskite architecture.^{18–25} Given the easy-to-obtain single crystal and good thermal stability of perovskite-like MOFs, they would be good candidates in the field of thermal conductivity research. Although there are several research studies available for the MOF materials,^{26–32}

thermal conductivity properties of perovskite-type MOFs remain unexplored.

Herein, we design and synthesize a new perovskite-type MOF to investigate the bulk crystal thermal conductivity properties of this type of material for the first time. *In situ* single crystal X-ray diffraction technology was employed to verify the phase stability of the perovskite-type MOF from 100 K to 300 K. The perovskite-type MOF crystal exhibits a low thermal conductivity of 1.3 W (K m)^{−1}, which is lower than most of the bulk crystal materials at room temperature.

The perovskite-type MOF was synthesized by mild solution methods. On layering a Co(NO₃)₂·6H₂O methanol solution onto a mixed solution of methanol, formic acid, and hydrazine monohydrate, the magenta rectangular crystals could be obtained after 24 hours. The mother solvent was exchanged with fresh methanol several times to clean the crystal surfaces. Single crystal X-ray diffraction (SCXRD) measurements indicated that the rectangular crystal was crystallized in the orthorhombic *Pna*2₁ space group with the formula [NH₂NH₃][Co(HCOO)₃] (**1**). As shown in Fig. 1a, eight Co²⁺ ions occupy the vertices of the lattice which are joined by formate ligands to construct a pcu topology (Fig. 1b) with cuboid cavities, whereas counter cations [NH₂NH₃]⁺ occupy the center of the cavities to give rise to a perovskite-type structure.

The crystal of perovskite-type MOF **1** exhibits good air-stability and thermal stability. As shown in Fig. 2 (right), the magenta rectangular crystals of **1** maintain good appearance

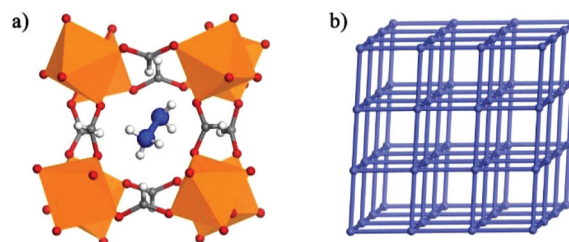


Fig. 1 (a) Perovskite structure of **1** (blue – nitrogen, white – carbon and yellow octahedra stand for CoO₆). (b) The pcu topology of **1** (cations have been omitted for clarity).

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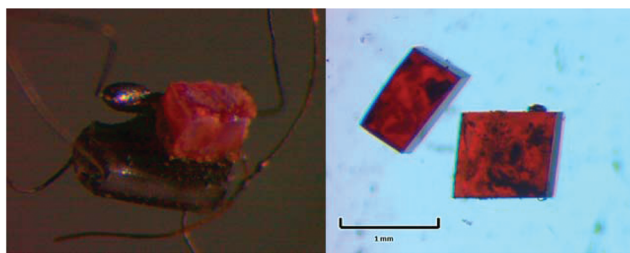


Fig. 2 The crystal of perovskite-type MOF 1 with the test wires (left) and the original crystal 1 (right).

after exposure to air for one week. The following SCXRD indicated that the structure of the single crystal of 1 undergoes no change during the exposure experiment. Furthermore, the curve of TGA shows that there is no weight loss for 1 before 433 K, suggesting the higher thermal stability of perovskite-type MOF crystals in comparison with conventional hybrid perovskite crystals which usually decompose below 373 K.^{5–7}

As shown in Fig. 2 (right), an intact ($1.2 \times 1.0 \times 0.5$ mm) crystal of 1 was selected for thermal conductivity measurement. The steady-state thermal conductivity of the cuboid shaped crystal along the *c*-direction was measured from 300 K to 12 K using a custom-designed radiation-shielded vacuum probe with an approximate 8% experimental uncertainty.^{33,34} The temperature-dependent thermal conductivity displays typical dielectric behavior; increases with the increase in temperature of up to 40 K, with a peak value of $2.5 \text{ W m}^{-1} \text{ K}^{-1}$, and then decreases up to the maximum measured temperature. Umklapp appears to be the dominant phonon-scattering mechanism above 40 K, as indicated by the $1/T$ behavior (the fit is shown in Fig. 3), while below 40 K the thermal conductivity has a T^3 temperature dependence indicative of the predominant boundary scattering of phonons.³⁴ This type of temperature dependence was also observed for MOF-5, where pore size plays an important role in affecting the phonon mean free path of the crystals.^{35–39} Compared with most bulk crystal materials, the room temperature thermal conductivity (1.3 W (K m)^{-1}) is very low (Table S6†) (Fig. 4).

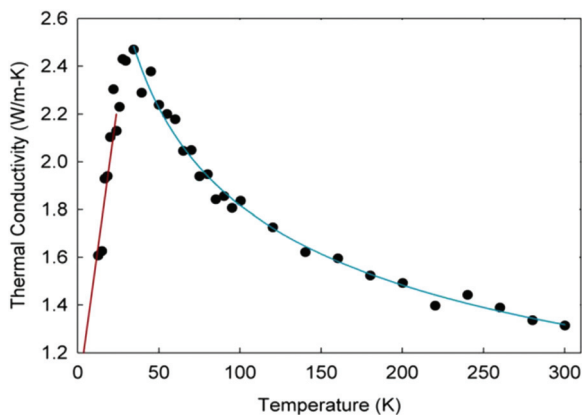


Fig. 3 Thermal conductivity of the perovskite MOF 1 crystal along the *c*-direction.

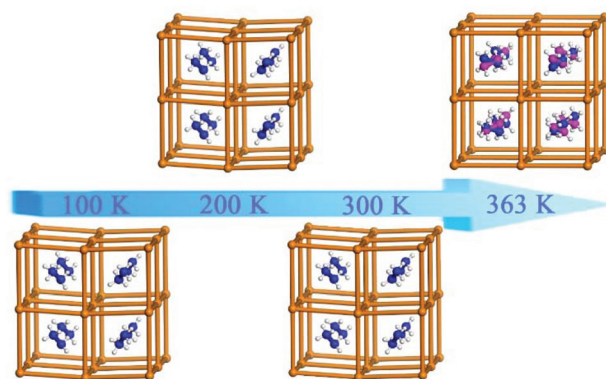


Fig. 4 The cations in perovskite-like MOF 1 at different temperatures.

The *in situ* variable-temperature SCXRD technology was employed to study the details of the possible phase transition of 1. Based on the results of thermal conductivity measurements, we chose 100 K, 200 K, and 300 K as the test temperatures to investigate the phase stability of 1. When the temperature increased from 100 K to 300 K, the space group of crystal 1 exhibited no change from $Pna2_1$, which indicated that there is no structure change between 100 K and 300 K. Interestingly, when the temperature continually increased to 363 K, the space group of crystal 1 changed from $Pna2_1$ to $Pnma$. The slightly distorted framework is straightened after the phase transition. The orientation of the $[\text{NH}_2\text{NH}_3]^+$ cation changed and affected the symmetry of the whole crystal. Cation disorder occurs in 1 at high temperatures and the symmetrical rotational movement of the NH_2 end of the $[\text{NH}_2\text{NH}_3]^+$ cation introduces another mirror plane to the structure, thus straightening it out. The *in situ* SCXRD results confirmed that there is no phase transition between 100 K and 300 K, which suggests that the structure undergoes no change when the thermal conductivity curve of 1 decreases.

In summary, we have presented the crystal thermal conductivity behavior of a perovskite-type MOF for the first time. Perovskite-like MOF 1 exhibits very low thermal conductivity of $1.30 \text{ W (K m)}^{-1}$ at room temperature, which is lower than most bulk crystal materials. The *in situ* SCXRD technology was used to verify the phase stability of perovskite-like MOF 1 between 100 K and 300 K. As one of the novel perovskite-type materials, the perovskite-type MOF exhibits broad prospects on the path of exploring new thermoelectric materials.

Conflicts of interest

There are no conflicts to declare.

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Notes and references

- G. J. Snyder and E. S. Toberer, *Nat. Mater.*, 2008, **7**, 105.
- G. Chen, M. S. Dresselhaus, G. Dresselhaus, J. P. Fleurial and T. Caillat, *Int. Mater. Rev.*, 2003, **48**, 45.
- L. E. Bell, *Science*, 2008, **321**, 1457.
- G. S. Nolas, J. W. Sharp and H. J. Goldsmid, *Thermoelectrics: Basics Principles and New Materials Developments*, Springer-Verlag, Berlin, 2001.
- M. Grätzel, *Acc. Chem. Res.*, 2017, **50**, 487.
- J. Burschka, N. Pellet, S.-J. Moon, R. Humphry-Baker, P. Gao, M. K. Nazeeruddin and M. Grätzel, *Nature*, 2013, **499**, 316.
- M. M. Lee, J. Teuscher, T. Miyasaka, T. N. Murakami and H. J. Snaith, *Science*, 2012, **338**, 643.
- Y. Song, S. Lv, X. Liu, X. Li, S. Wang, H. Wei, D. Li, Y. Xiao and Q. Meng, *Chem. Commun.*, 2014, **50**, 15239.
- K. Eckhardt, V. Bon, J. Getzschmann, J. Grothe, F. M. Wisser and S. Kaskel, *Chem. Commun.*, 2016, **52**, 3058.
- T. Ye, X. Wang, X. Li, A. Q. Yan, S. Ramakrishna and J. Xu, *J. Mater. Chem. C*, 2017, **5**, 1255.
- A. Pisoni, J. Jacimovic, O. S. Barisic, M. Spina, R. Gaál, L. Forró and E. Horváth, *J. Phys. Chem. Lett.*, 2014, **5**, 2488.
- S. Sun, Z. Deng, Y. Wu, F. Wei, F. Isikgor, F. Brivio, M. Gaultois, J. Ouyang, P. Bristowe, T. Cheetham and G. Kieslich, *Chem. Commun.*, 2017, **53**, 7537.
- S. D. Stranks, G. E. Eperon, G. Grancini, C. Menelaou, M. J. P. Alcocer, T. Leijtens, L. M. Herz, A. Petrozza and H. J. Snaith, *Science*, 2013, **342**, 341.
- A. R. Millward and O. M. Yaghi, *J. Am. Chem. Soc.*, 2005, **127**, 17998.
- J.-R. Li, R. J. Kuppler and H.-C. Zhou, *Chem. Soc. Rev.*, 2009, **38**, 1477.
- J. Lee, O. K. Farha, J. Roberts, K. A. Scheidt, S. T. Nguyen and J. T. Hupp, *Chem. Soc. Rev.*, 2009, **38**, 1450.
- L. E. Kreno, K. Leong, O. K. Farha, M. Allendorf, R. P. Van Duyne and J. T. Hupp, *Chem. Rev.*, 2012, **112**, 1105.
- M. Mączka, A. Pietraszko, B. Macalik and K. Hermanowicz, *Inorg. Chem.*, 2014, **53**, 787.
- A. Ciupa, M. Mączka, A. Gagor, A. Sieradzki, J. Trzmiel, A. Pikul and M. Ptak, *Dalton Trans.*, 2015, **44**, 8846.
- S. Chen, R. Shang, B.-W. Wang, Z.-M. Wang and S. Gao, *Angew. Chem., Int. Ed.*, 2015, **127**, 11245.
- L. C. Gómez-Aguirre, B. Pato-Doldán, J. Mira, S. Castro-García, M. A. Señaris-Rodríguez, M. Sánchez-Andújar, J. Singleton and V. S. Zapf, *J. Am. Chem. Soc.*, 2016, **138**, 1122.
- N. Abhyankar, S. Bertaina and N. S. Dalal, *J. Phys. Chem.*, 2015, **119**, 28143.
- T. M. Zhao, S. Chen, R. Shang, B.-W. Wang, Z.-M. Wang and S. Gao, *Inorg. Chem.*, 2016, **55**, 10075.
- R. Shang, G.-C. Xu, Z.-M. Wang and S. Gao, *Chem. – Eur. J.*, 2014, **20**, 1146.
- M. Mączka, A. Ciupa, A. Gagor, A. Sieradzki, A. Pikul, B. Macalik and M. Drozd, *Inorg. Chem.*, 2014, **53**, 5260.
- T. A. Semelsberger, M. Veenstra and C. Dixon, *Int. J. Hydrogen Energy*, 2016, **41**, 4690.
- H. Wang, Z. Qu, W. Zhang and W. Tao, *Computation*, 2015, **3**, 558.
- X. Wang, R. Guo, D. Xu, J. Chung, M. Kaviani and B. Huang, *J. Phys. Chem. C*, 2015, **119**, 26000.
- K. J. Erickson, F. Léonard, V. Stavila, M. E. Foster, C. D. Spataru, R. E. Jones, B. M. Foley, P. E. Hopkins, M. D. Allendorf and A. A. Talin, *Adv. Mater.*, 2015, **27**, 3453.
- L. Han, B. Makenzie and P. A. Greaney, *Comput. Mater. Sci.*, 2014, **94**, 292.
- X. Zhang and J. Jiang, *J. Phys. Chem. C*, 2013, **117**, 18441.
- J. Purewal, D. Liu, A. Sudik, M. Veenstra, J. Yang, S. Maurer and D. J. Siegel, *J. Phys. Chem. C*, 2012, **116**, 20199; M. I. Nandasiri, J. Liu, B. P. McGrail, J. Jenks, H. T. Schaefer, V. Shutthanandan, Z. Nie, P. F. Martin and S. K. Nune, *Sci. Rep.*, 2016, **6**, 27805.
- J. Martin and G. S. Nolas, *Rev. Sci. Instrum.*, 2016, **87**, 15105.
- J. Martin, S. Erickson, G. S. Nolas, P. Alboni, T. M. Tritt and J. Yang, *J. Appl. Phys.*, 2006, **99**, 44903.
- J. Callaway, *Phys. Rev.*, 1959, **113**, 1046.
- B. L. Huang, Z. Ni, A. Millward, A. J. H. McGaughey, C. Uher, M. Kaviani and O. Yaghi, *Int. J. Heat Mass Transfer*, 2007, **50**, 405.
- D. Liu, J. J. Purewal, J. Yang, A. Sudik, S. Maurer, U. Mueller, J. Ni and D. J. Siegel, *Int. J. Hydrogen Energy*, 2012, **37**, 6109.
- B. L. Huang, Z. Ni, A. Millward, A. J. H. McGaughey, C. Uher, M. Kaviani and O. Yaghi, *Int. J. Heat Mass Transfer*, 2007, **50**, 393.
- H. Babaei, A. J. McGaughey and C. E. Wilmer, *Chem. Sci.*, 2017, **8**, 583.