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Intrinsic zero thermal expansion in cube cyanurate $K_6Cd_3(C_3N_3O_3)_4$ $\frac{HPSTAR}{829-2019}$

Mingjun Xia, ()*^{‡a,b} Fei Liang, ()^{‡a} Xianghe Meng, ()^{a,b} Yonggang Wang ()^c and Zheshuai Lin^a

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Zero thermal expansion (ZTE) materials are rare, but have intriguing properties which can be used in precise optical devices to prevent thermal fluctuation. Here, a new cube ZTE compound $K_6Cd_3(C_3N_3O_3)_4$, composed of conjugated $[C_3N_3]$ rigid six-membered-rings and $[CdN_4]$ tetrahedra, has been reported for the first time. Its thermal expansion coefficient is as small as 0.06 MK⁻¹, which is one-order of magnitude lower than that of the commercially available Invar alloy. In addition, the ZTE mechanism was elucidated using first-principles calculations.

Zero thermal expansion (ZTE) materials, that neither expand nor contract with temperature changes, can be free from the thermally induced stress resulting from thermal fluctuation.¹ In recent years, isotropic ZTE materials have received significant attention owing to their wide spread applications in high precision instruments, optical devices, thermomechanical actuators and micro systems used in environments which may experience thermal shock.² Generally, there are two routes used to achieve the ZTE effect in functional materials: (i) mixing negative thermal expansion (NTE) and positive thermal expansion (PTE) compounds together in an appropriate ratio;³ and (ii) chemically doping NTE compounds in order to produce materials with a zero coefficient of thermal expansion (CTE).⁴ Both of these methods may experience thermal mismatch of the materials and thermal stress.⁵ In comparison, intrinsic ZTE is a perfect choice which does not require any chemical modification.⁶ So far, a few ZTE materials have been reported including Invar alloys,7 PbTiO3-based perovskites,8 $Sc_{1-x}M_xF_3$ (M = Ga, Fe),⁹ ZrMgMo₃O₁₂,⁶ ZnZrF₆,¹⁰ Prussian blue Fe[Co(CN)₆],^{6a} Zn₄B₆O₁₃ (ZBO),¹¹ SnO₂ nanowires,¹² and so forth. As is well known, isotropic materials, which crystallize in a cube crystal system, are beneficial for practical applications. Notably, intrinsic isotropic ZTE compounds are very rare. The search for

^aBeijing Center for Crystal Research and Development, Key Laboratory of Functional Crystals and Laser Technology, Technical Institute of Physics and Chemistry, Chinese Academy of Sciences, Beijing 100190, P.R. China. E-mail: xiamingjun@mail.ipc.ac.cn ^bCenter of Materials Science and Optoelectronics Engineering, University of Chinese Academy of Sciences, Beijing 100049, P.R. China ZTE materials is challenging, especially for single-phase ZTE materials crystallizing in a cubic crystal structure.

In previously published studies, the linear cyanide [CN]⁻ unit was proposed as a fundamental anion for NTE and ZTE materials owing to its short bond length distance (about 1.16 Å) and high rigidity in crystals such as Zn(CN)2,13 Cd (CN)₂,¹⁴ Ag₃[Co(CN)₆],^{3a} Zn[Au(CN)₂]₂,¹⁵ LaCo(CN)₆,¹⁶ and YFe (CN)₆.^{3b} Theoretical studies demonstrated that the transverse acoustic modes of the [CN]⁻ unit give rise to a relatively sharp feature at about 2-4 meV in the phonon density of states, relating to large negative Grüneisen parameters, indicating that they are the primary contributors to the negative thermal expansion in the materials.¹⁷ In 2013, an article was published demonstrating that $Cd(H_3C_3N_2)_2$, containing five-membered imidazolate [C₃N₂] rings, exhibits one-dimensional NTE behavior along the b axis.¹⁸ The fundamental mechanical response from the linear $[CN]^-$ unit is also mirrored in the $[C_3N_2]$ ring units. Therefore, there is still an attraction to searching for anomalous NTE or ZTE materials in other C-N systems.

The cyanuric group $[C_3N_3O_3]^{3-}$ is a common type of C-N coordination ion with a [C3N3] ring and three terminal O atoms linked to the C atom.¹⁹ Recently, Meyer's group synthesized several metal cyanurates via a cyclotrimerization reaction from a linear cyanate [CNO]⁻ group in a fused silica tube.²⁰ The planar [C₃N₃O₃]³⁻ group, which is isoelectric to the $[B_3O_6]^{3-}$ anion, is considered to be an excellent construction block for ultraviolet nonlinear optical (NLO) and birefringent crystals owing to its strong conjugated interaction and optical anisotropy.²¹ Accordingly, several new metal cyanurates were found, including $Ba_2M(C_3N_3O_3)_2$ (M = Mg, Ca, Ba),²² Na₃(C₃N₃O₃),²³ K₆Cd₃(C₃N₃O₃)₄ (KCCY)²⁴ and the hydroisocyanurates $K_2(HC_3N_3O_3)^{25}$ $LiCl(H_{3}C_{3}N_{3}O_{3}),^{26}$ KLi(HC₃N₃O₃)·2H₂O (KLHCY)²⁷ and Cs₃Na(H₂C₃N₃O₃)₄·3H₂O (CNHCY).²⁸ In particular, KLHCY and CNHCY are potential



^cCenter for High Pressure Science and Technology Advanced Research (HPSTAR), Beijing, 100094, P.R. China

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[‡]These authors contributed equally.

NLO crystals for the fourth-harmonic-generation of Nd-based lasers. To the best of our knowledge, there are no reports published which focus on the thermal behaviors of metal cyanurates. Among these compounds, KCCY is a special one featuring a unique diamond-like framework built from a $[CdN_4]$ tetrahedra and $[C_3N_3]$ six-membered-rings (6-MRs), which is very similar to that of the basic NTE model in $Cd(CN)_2$. More importantly, it crystallizes in a cube structure lattice. Guided by this idea, the thermal expansion of KCCY was systematically investigated, and surprisingly the measured linear thermal expansion coefficient was found to be as small as 0.06 MK⁻¹ over a broad temperature range of 10–130 K. Herein, we propose KCCY as a new cube single-phase ZTE material with a diamond structure based on the combined study of the experimental investigation and first principles calculations.

KCCY belongs to the cubic space group $I\bar{4}3d$ and features a complicated three dimensional framework (Fig. 1a).²⁴ Every Cd



Fig. 1 (a) Three dimensional crystal structure of KCCY; (b) and (c) coordination environment of the $[CdN_4]$ tetrahedron and planar $[C_3N_3]$ 6-MR.

atom is connected by four $[C_3N_3]$ rings by sharing the corner N atoms (Fig. 1b) and each $[C_3N_3]$ ring is linked to three equivalent $[CdN_4]$ tetrahedra. The C–N bond distances in the $[C_3N_3]$ 6-MRs are 1.365 Å and 1.372 Å, respectively. The Cd–N bond length is 2.252 Å, which is comparable to that in Cd $(CN)_2$ (2.195 Å)¹⁷ and Cd $(H_3C_3N_2)_2$ (2.177–2.217 Å).¹⁸ Clearly, the $[C_3N_3]$ ring in the cyanurate group is tightly locked by the $[CdN_4]$ tetrahedra, while the dangling O atom is relatively flexible. K atoms occupy the voids in the three dimensional framework to maintain the charge balance.

The intrinsic lattice thermal expansion of KCCY over the temperature range of 10–300 K was investigated using variable temperature X-ray diffraction (XRD). The XRD patterns revealed that no new peaks appeared at any of the measured temperatures and that all diffraction peaks can be indexed using the cubic $I\bar{4}3d$ space group (Fig. S1†). To further determine accurate cell parameters, all XRD patterns were refined using the Rietveld method. As shown in Fig. 2, the refined plots of KCCY at different temperatures converged very well, indicating that our synthesized samples were pure and stable over the measured temperature range. In addition, all of the structures belong to the cubic system and thus, their thermal expansions are isotropic over the entire temperate range. The refined lattice constants for the range from 10 to 300 K are listed in Table S1.†

As shown in Fig. 3, the linear thermal expansion coefficient of KCCY displays a change at the turning point of 130 K. At temperatures below 130 K, KCCY is a ZTE material with an ultralow thermal expansion coefficient of 0.06 MK⁻¹. This value is much lower than those of borate ZBO (0.28 MK⁻¹, 13–110 K),¹¹ Fe[Co(CN)₆] (-1.47 MK⁻¹, 4.2–300 K)^{6a} and TaO₂F (0.6 MK⁻¹, 200–773 K).^{6b} The lattice constant of KCCY significantly increases with the rising temperature above 130 K. The average thermal expansion coefficient from 130 to 300 K is 9.03 MK⁻¹, which can be accurately cataloged to PTE. As



Fig. 2 The refinement plots for the XRD patterns of KCCY at: (a) 10 K, (b) 70 K, (c) 150 K and (d) 250 K, respectively.



Fig. 3 Variation of the refined lattice constants of KCCY (inset shows the evolution of the (008) peak as the temperature changes).

observed in the inset in Fig. 3, the (008) peak Bragg reflection remains in almost the same position in the temperature range of 10–130 K, and moves to small angles when the temperature reaches room temperature. This is in good agreement with the refined parameters. Accordingly, the unit cell volume evolution with temperature for KCCY exhibits a similar behavior owing to the isotropic point group (Fig. S2†). To the best of our knowledge, the CTE of KCCY is the smallest among the cube oxides.

In order to gain a deeper insight into the mechanism of ZTE in KCCY, we performed ab initio calculations on the lattice vibrational behaviors. Firstly, the optimized lattice constant (13.156 Å) was found to be very close to the experimental value obtained (13.401 Å) with a relative difference below 2%. Based on the optimized crystal structure, the calculated phonon spectrum exhibits no imaginary mode with a negative vibrational frequency, thus suggesting KCCY is kinetically stable (Fig. S3[†]). Moreover, the simulated infrared (IR) peaks are perfectly consistent with the measured spectrum obtained (Fig. S4[†]), in which the peaks located at 621, 1138, 1417 and 1518 cm⁻¹ were assigned to the stretching modes and the peaks around 821 cm⁻¹ were attributed to the bending modes of the $[C_3N_3O_3]^{3-}$ group, respectively.²⁹ Therefore, the calculated parameters were accurate enough to simulate the lattice vibrations of KCCY.

In the initially reported work, the near-ZTE of ZBO at low temperature was explained by the specific behavior of the phonon modes at low frequencies. In the present study, we considered the ZTE behavior in KCCY using similar analysis. First, the Cd–N bond length (2.25 Å) was found to be longer than that of the C–N bond (1.36 Å) and the Mulliken population³⁰ is smaller (0.35 vs. 0.98), suggesting that the [C₃N₃] ring shows strong covalence. The [C₃N₃] linker groups can be viewed as almost rigid rings because their internal stretch frequency is about 80 meV (Fig. S5†), which greatly exceeds the other frequencies in the unit cell. A conventional unit cell of KCCY contains 180 atoms, corresponding to 540 degrees of

freedom in the first Brillouin zone. The irreducible representation of the $I\bar{4}3d$ space group at the Γ -point yields a sum of Γ = 84E + 20A1 + 22A2 + 204T1 + 210T2 phonon modes. As mentioned previously, the thermal expansion coefficient of KCCY exhibits an abrupt change at 130 K, equal to a phonon energy of 11.26 meV according to the Boltzmann law and a vibrational frequency of 91 cm⁻¹. Furthermore, the phonon state intensity also displays a clear fluctuation around 85 cm⁻¹, which is well matched with the experimental results. Therefore, the anomalous ZTE in KCCY could be attributed to special vibrational modes at low frequency. Further vibrational analysis reveals that the phonon modes undergo the following evolution of three atomic vibration types with increasing frequency $(40-140 \text{ cm}^{-1})$: (i) below 50 cm⁻¹ (only a representative mode is plotted), the phonon mode I is predominantly attributed to the sliding displacement of K^+ (Fig. 4b); (ii) 50–90 cm⁻¹, the vibrational mode II is mainly assigned to the bending vibrations of the C-O bonds and the additional sliding of K⁺. Both of these two types experience few contributions from the C-N bonds and Cd-N bonds. As a result, the three-dimensional framework built using the $[C_3N_3]$ ring and $[CdN_4]$ remains almost immobile and contributes very little to the thermal expansion.

When there is a gradual increase in the phonon frequency to more than 90 cm⁻¹, the C, N and Cd atoms start to participate in holistic vibrations. For instance, the phonon mode (III) at 105 cm⁻¹ is composed of out-plane [C_3N_3] bending, C–O bond stretching vibrations and K⁺ displacement. The coopera-



Fig. 4 (a) Partial density of phonon states of KCCY and (b) vibrational modes at 50 (I), 70 (II), 105 (III), and 115 (IV) cm⁻¹; the purple, pink, grey, blue and red spheres represent K, Cd, C, N, O, respectively. The green vectors indicate the relative atomic vibrational directions.

tive vibrations (IV) at 115 cm⁻¹ contain in-plane $[C_3N_3]$ rotations, C-O bond bending and an additional K⁺ sliding mode. Evidently, these high frequency phonons will bring about variations in the Cd-N and C-N bond lengths which cannot be ignored, thus leading to significantly increased thermal expansion coefficients. It is interesting to compare the three compounds of Cd(CN)₂, Cd(H₃C₃N₂)₂ and KCCY with the abnormal thermal expansion properties. As depicted in Fig. S6,^{\dagger} Cd(CN)₂ and KCCY belong to the cubic system while $Cd(H_3C_3N_2)_2$ belongs to the orthogonal system. In $Cd(CN)_2$, the [CdN₄] and [CdC₄] tetrahedra are connected through the C-N dimers. Therefore, the transverse vibrational degree perpendicular to the Cd-C-N-Cd chain is still maintained. Furthermore, two $[CdN_4]$ tetrahedra are linked by a $[C_3N_2]$ fivemembered-ring in $Cd(H_3C_3N_2)_2$. Accordingly, the transverse vibrational degree is partially maintained along the N-N line. In KCCY, three $[CdN_4]$ tetrahedra are connected by the $[C_3N_3]$ 6-MRs and the transverse vibrational degree is almost completely limited along the diagonal C-N line, except for several outplane vibrational modes. As is well known, a triangle is more stable and robust. Therefore, KCCY exhibits special ZTE, but not NTE, behavior as observed in $Cd(CN)_2$ and $Cd(H_3C_3N_2)_2$.

conclusion, a new isotropic ZTE In cyanurate $K_6Cd_3(C_3N_3O_3)_4$ was reported for the first time. Its thermal expansion coefficient is only 0.06 MK⁻¹ in a broad temperature range from 10 to 130 K. The relationship between the anomalous ZTE and phonon vibrations was also determined using theoretical calculations. This work proposes the delocalized $[C_3N_3]$ rigid ring as a modern building unit for anomalous expansion materials and provides a novel platform for the discovery of more single-phase NTE and ZTE materials in the metal cyanurates. The high-pressure response of the title compound is also attractive and related work is in progress.

Conflicts of interest

The authors declare no competing financial interests.

Acknowledgements

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Notes and references

 (a) T. A. Mary, J. S. O. Evans, T. Vogt and A. W. Sleight, *Science*, 1996, 272, 90–92; (b) J. Chen, L. Hu, J. X. Deng and X. R. Xing, *Chem. Soc. Rev.*, 2015, 44, 3522–3567.

- 2 (a) C. A. Perottoni and J. A. H. da Jornada, *Science*, 1998, 280, 886–890; (b) J. R. Salvador, F. Guo, T. Hogan and M. G. Kanatzidis, *Nature*, 2003, 425, 702–706.
- 3 (a) A. L. Goodwin, M. Calleja, M. J. Conterio, M. T. Dove, J. S. O. Evans, D. A. Keen, L. Peters and M. G. Tucker, *Science*, 2008, 319, 794–797; (b) Q. Gao, J. Chen, Q. Sun, D. Chang, Q. Huang, H. Wu, A. Sanson, R. Milazzo, H. Zhu, Q. Li, Z. Liu, J. Deng and X. Xing, *Angew. Chem., Int. Ed.*, 2017, 56, 9023–9028; (c) V. V. Atuchin, F. Liang, S. Grazhdannikov, L. I. Isaenko, P. G. Krinitsin, M. S. Molokeev, I. P. Prosvirin, X. Jiang and Z. Lin, *RSC Adv.*, 2018, 8, 9946–9955.
- 4 (a) B. K. Greve, K. L. Martin, P. L. Lee, P. J. Chupas,
 K. W. Chapman and A. P. Wilkinson, *J. Am. Chem. Soc.*,
 2010, 132, 15496–15498; (b) A. E. Phillips and A. D. Fortes, *Angew. Chem., Int. Ed.*, 2017, 56, 15950–15953.
- 5 K. Lin, H. Wu, F. Wang, Y. Rong, J. Chen, J. Deng, R. Yu,
 L. Fang, Q. Huang and X. Xing, *Dalton Trans.*, 2014, 43, 7037–7043.
- 6 (a) S. Margadonna, K. Prassides and A. N. Fitch, J. Am. Chem. Soc., 2004, 126, 15390-15391; (b) J. Z. Tao and A. W. Sleight, J. Solid State Chem., 2003, 173, 45-48; (c) C. P. Romao, F. A. Perras, U. Werner-Zwanziger, J. A. Lussier, K. J. Miller, C. M. Calahoo, J. W. Zwanziger, M. Bieringer, B. A. Marinkovic, D. L. Bryce and M. A. White, Chem. Mater., 2015, 27, 2633-2646.
- 7 M. van Schilfgaarde, I. A. Abrikosov and B. Johansson, *Nature*, 1999, **400**, 46–49.
- 8 J. Chen, X. Xing, C. Sun, P. Hu, R. Yu, X. Wang and L. Li, *J. Am. Chem. Soc.*, 2008, **130**, 1144–1145.
- 9 J. Chen, Q. Gao, A. Sanson, X. Jiang, Q. Huang, A. Carnera, C. G. Rodriguez, L. Olivi, L. Wang, L. Hu, K. Lin, Y. Ren, Z. Lin, C. Wang, L. Gu, J. Deng, J. P. Attfield and X. Xing, *Nat. Commun.*, 2017, 8, 14441.
- 10 L. Hu, J. Chen, J. Xu, N. Wang, F. Han, Y. Ren, Z. Pan, Y. Rong, R. Huang, J. Deng, L. Li and X. Xing, *J. Am. Chem. Soc.*, 2016, **138**, 14530–14533.
- X. X. Jiang, M. S. Molokeev, P. F. Gong, Y. Yang, W. Wang, S. H. Wang, S. F. Wu, Y. X. Wang, R. J. Huang, L. F. Li, Y. C. Wu, X. R. Xing and Z. S. Lin, *Adv. Mater.*, 2016, 28, 7936–7940.
- 12 H. Zhu, Q. Li, C. Yang, Q. Zhang, Y. Ren, Q. Gao, N. Wang, K. Lin, J. Deng, J. Chen, L. Gu, J. Hong and X. Xing, *J. Am. Chem. Soc.*, 2018, **140**, 7403–7406.
- 13 (a) K. W. Chapman, P. J. Chupas and C. J. Kepert, J. Am. Chem. Soc., 2005, 127, 15630–15636; (b) K. W. Chapman and P. J. Chupas, J. Am. Chem. Soc., 2007, 129, 10090–10091.
- 14 (a) A. L. Goodwin and C. J. Kepert, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2005, 71, 140301; (b) A. L. Goodwin, *Phys. Rev. B*, 2006, 74, 134302.
- 15 A. B. Cairns, J. Catafesta, C. Levelut, J. Rouquette, A. van der Lee, L. Peters, A. L. Thompson, V. Dmitriev, J. Haines and A. L. Goodwin, *Nat. Mater.*, 2013, **12**, 212–216.
- 16 S. G. Duyker, V. K. Peterson, G. J. Kearley, A. J. Ramirez-Cuesta and C. J. Kepert, *Angew. Chem., Int. Ed.*, 2013, 52, 5266–5270.

- 17 J. W. Zwanziger, Phys. Rev. B: Condens. Matter Mater. Phys., 2007, 76, 052102.
- 18 I. E. Collings, A. B. Cairns, A. L. Thompson, J. E. Parker, C. C. Tang, M. G. Tucker, J. Catafesta, C. Levelut, J. Haines, V. Dmitriev, P. Pattison and A. L. Goodwin, *J. Am. Chem. Soc.*, 2013, 135, 7610–7620.
- 19 E. H. Wiebenga and N. F. Moerman, *Nature*, 1938, **141**, 122–122.
- 20 (a) M. Kalmutzki, M. Stroebele and H. J. Meyer, *Dalton Trans.*, 2013, 42, 12934–12939; (b) M. Kalmutzki, M. Strobele, F. Wackenhut, A. J. Meixner and H. J. Meyer, *Angew. Chem., Int. Ed.*, 2014, 53, 14260–14263; (c) M. Kalmutzki, M. Strobele, F. Wackenhut, A. J. Meixner and H. J. Meyer, *Inorg. Chem.*, 2014, 53, 12540–12545.
- 21 F. Liang, L. Kang, X. Zhang, M. Lee, Z. Lin and Y. Wu, *Cryst. Growth Des.*, 2017, **17**, 4015–4020.
- 22 (a) Z. Li, F. Liang, Y. Guo, Z. Lin, J. Yao, G. Zhang, W. Yin,
 Y. Wu and C. Chen, *J. Mater. Chem. C*, 2018, 6, 12879–12887; (b) J. Tang, F. Liang, X. Meng, K. Kang, W. Yin,

T. Zeng, M. Xia, Z. Lin, J. Yao, G. Zhang and B. Kang, *Cryst. Growth Des.*, 2019, **19**, 568–572.

- 23 P. Gross and H. A. Höppe, Z. Anorg. Allg. Chem., 2019, 645, 257–266.
- 24 M. Xia, M. Zhou, F. Liang, X. Meng, J. Yao, Z. Lin and R. Li, *Inorg. Chem.*, 2018, 57, 32–36.
- 25 N. Wang, F. Liang, Y. Yang, S. Zhang and Z. Lin, *Dalton Trans.*, 2019, **48**, 2271–2274.
- 26 F. Liang, N. Wang, X. Liu, Z. Lin and Y. Wu, Chem. Commun., 2019, 55, 6257-6260.
- 27 D. Lin, M. Luo, C. Lin, F. Xu and N. Ye, *J. Am. Chem. Soc.*, 2019, **141**, 3390–3394.
- 28 X. Meng, F. Liang, J. Tang, K. Kang, Q. Huang, W. Yin, Z. Lin and M. Xia, *Eur. J. Inorg. Chem.*, 2019, 2019, 2791– 2795.
- 29 M. Kalmutzki, M. Ströbele, H. F. Bettinger and H. J. Meyer, *Eur. J. Inorg. Chem.*, 2014, 2014, 2536–2543.
- 30 A. E. Reed, R. B. Weinstock and F. Weinhold, J. Chem. Phys., 1985, 83, 735-746.