Zero thermal expansion (ZTE) materials are rare, but have intriguing properties which can be used in precise optical devices to prevent 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 Sc1−xMxF3 (M = Ga, Fe),9 ZrMgMo3O12,6c ZnZrF6,10 Prussian blue Ag3[Co(CN)6],3d 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(H2C2N2)2, containing five-membered imidazolato [C3N3] 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 [C3N3] ring units. Therefore, there is still an attraction to searching for anomalous NTE or ZTE materials in other C–N systems.

The cyanuric group [C3N3O3]− 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]2− group, which is isoelectronic to the [B2O6]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 Ba2M(C3N3O3)2 (M = Mg, Ca, Ba),24 Na3(C3N3O3)2,25 K2Cd3(C3N3O3)4 (KCCY)24 and the hydroxo cyanurates K3(H2C3N3O3)2,25 LiCl(H2C3N3O3)2,26 KLi(HC3N3O3)2:2H2O (KLHCY)27 and Cs2Na(H2C3N3O3)2:3H2O (CNHCY).28 In particular, KLHCY and CNHCY are potential...
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 cyanates. Among these compounds, KCCY is a special one featuring a unique diamond-like framework built from a \([\text{CdN}_4]\) tetrahedra and \([\text{C}_3\text{N}_3]\) six-membered-rings (6-MRs), which is very similar to that of the basic NTE model in \(\text{Cd(CN)}_2\). 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 \(\text{I}4\bar{1}3d\) and features a complicated three dimensional framework (Fig. 1a).\(^{24}\) Every Cd atom is connected by four \([\text{C}_3\text{N}_3]\) rings by sharing the corner N atoms (Fig. 1b) and each \([\text{C}_3\text{N}_3]\) ring is linked to three equivalent \([\text{CdN}_4]\) tetrahedra. The C–N bond distances in the \([\text{C}_3\text{N}_3]\) 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 \(\text{Cd(CN)}_2\) (2.195 Å)\(^{17}\) and \(\text{Cd(H}_2\text{C}_2\text{N}_2)_2\) (2.177–2.217 Å).\(^{18}\) Clearly, the \([\text{C}_3\text{N}_3]\) ring in the cyanurate group is tightly locked by the \([\text{CdN}_4]\) 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 \(\text{I}4\bar{1}3d\) space group (Fig. S1\(^{\dagger}\)). 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.\(^{\dagger}\)

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 TaO\(_2\)F (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
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 [C₃N₃O₃]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 population 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 H₄d space group at the Γ-point yields a sum of \( \Gamma = 84E + 20A1 + 22A2 + 204T1 + 210T2 \) 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 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 [C₃N₃] ring and [CdN₄] 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 [C₃N₃] bending, C–O bond stretching vibrations and K⁺ displacement. The coopera-
tive vibrations (IV) at 115 cm⁻¹ contain in-plane [C₃N₄] 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, Cd(CN)₂ and Cd(H₃C₃N₂)₂ belong to the orthogonal system while Cd(H₃C₃N₂)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 [CdN₄] tetrahedra are linked by a [C₃N₃] five-membered-ring in Cd(H₃C₃N₂)₂. Accordingly, the transverse vibrational degree is partially maintained along the N–N line. In KCCY, three [CdN₄] tetrahedra are connected by the [C₃N₃] 6-MRs and the transverse vibrational degree is almost completely limited along the diagonal C–N line, except for several out-of-plane 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(H₃C₃N₂)₂.

In conclusion, a new isotropic ZTE cyanurate K₆Cd₃(C₃N₃O₃)₄ was reported for the first time. Its thermal expansion coefficients are 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 [C₃N₄] 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.

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Notes and references


