Supporting Information

Intrinsic zero thermal expansion in cube cyanurate $K_6Cd_3(C_3N_3O_3)_4$

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1. Sample synthesis

Polycrystalline samples of $K_6Cd_3(C_3N_3O_3)_4$ were obtained by traditional solid state reaction in a stoichiometric mixture of $CdCl_2$ and KCNO. The mixtures were carefully ground and loaded into fused-silica tube. And the tube was flame-sealed under a high vacuum of 10^{-3} Pa and placed in a computer-controlled furnace. The furnace was slowly heated to 673 K within 6 h and left for 72 h, then cooled to room temperature by switching off the furnace. Finally, the crystalline products were washed by methanol to remove the chloride.

2. Characterization

The temperature dependence of X-ray diffraction patterns were collected on a Rigaku Smartlab 9 KW X-ray diffractometer with Cu Kα radiation in the temperature range from the 10 K to 300 K with the internal of 20 K. The angular scanning range is from 10° to 80° with a step of 0.02° and scanning speed 10°/min. The temperature was controlled Helium-4 compression refrigerator and monitored by Lakeshore cryotronics Model 335 with the accuracy of 0.1 K. The cell parameters under different temperature were refined by Rietveld method using the cubic symmetry ($I\bar{4}3d$) by the *Fullprof* program.

Infrared (IR) spectroscopy was collected on a Varian Excalibur 3100 spectrometer in the 400 – 4000 cm-1 range. The $K_6Cd_3(C_3N_3O_3)_4$ and KBr samples with mass ratio about 1:100 were mixed thoroughly.

3. Computational method

The first-principles calculations at the atomic level for $K_6Cd_3(C_3N_3O_3)_4$ crystal were performed by density functional theory (DFT)[1], which has been successfully applied on metal cyanurates.[2] The exchange–correlation (XC) functionals were described by the local density approximation (LDA)[3] and the ion-electron interactions were modeled by the norm conversing pseudopotentials[4] for all elements. In this model, K $3s^23p^64s^1$, Cd $4d^{10}5s^2$, C $2s^22p^2$, N $2s^22p^3$ and O $2s^22p^4$ electrons were treated as the valence electrons, respectively. The kinetic energy cutoff of 900 eV and dense k-point meshes[5] (4×4×4) spanning less than $0.04 Å^{-3}$ in the Brillouin zone were chosen to ensure the sufficient accuracy of the calculated results. In addition, the linear response method[6] based on quasi-harmonic approximation was employed to obtain the phonon dispersion of titled crystal. All of vibrational modes were assigned based on *Vibrational Analysis Module* in *CASTEP*.[7] In order to clearly elucidate the distinct contribution from constituent atoms for phonon vibrations, only a zooming out block containing three K cations, one ($C_3N_3O_3$) and three (CdN_4) anionic groups were highlighted.

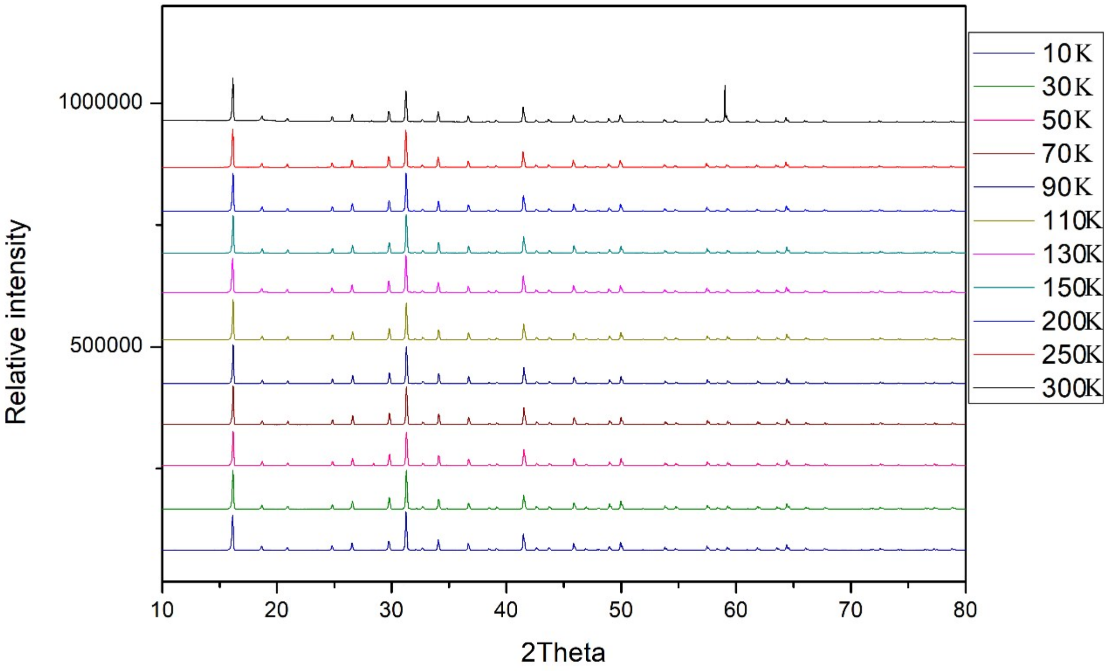

Figure S1. XRD patterns of $K_6Cd_3(C_3N_3O_3)_4$ at various temperatures.

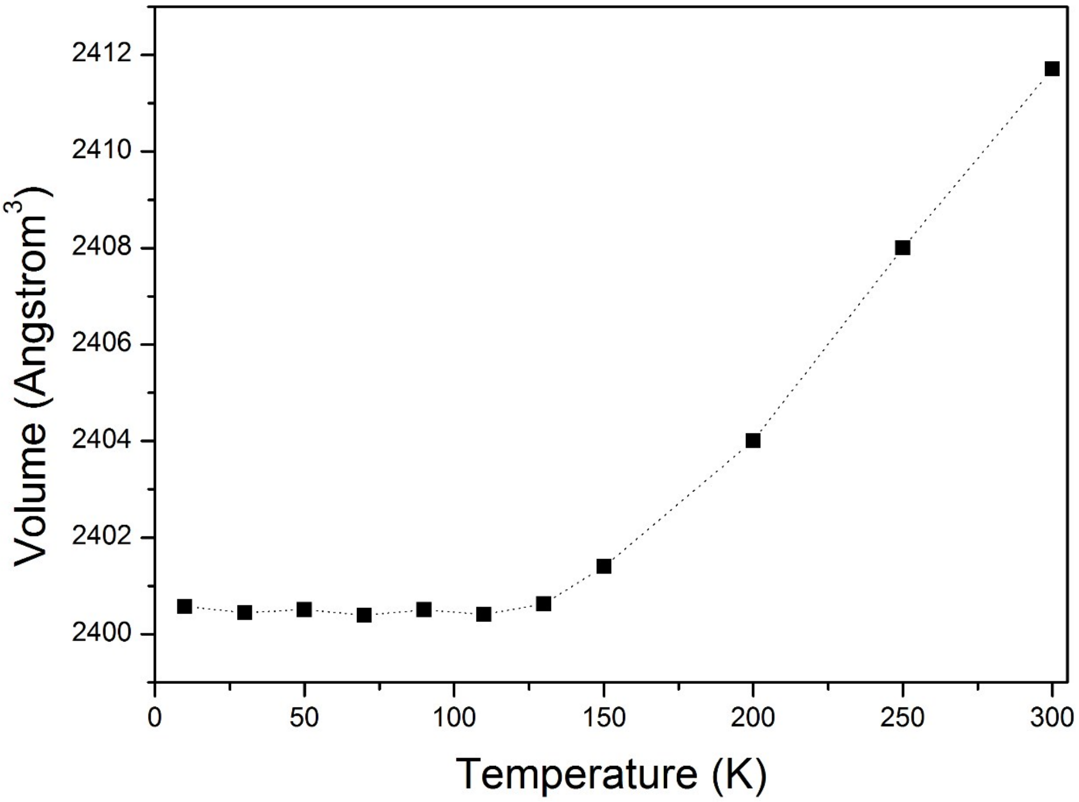

Figure S2. Unit cell volume evolution as a function of temperature.

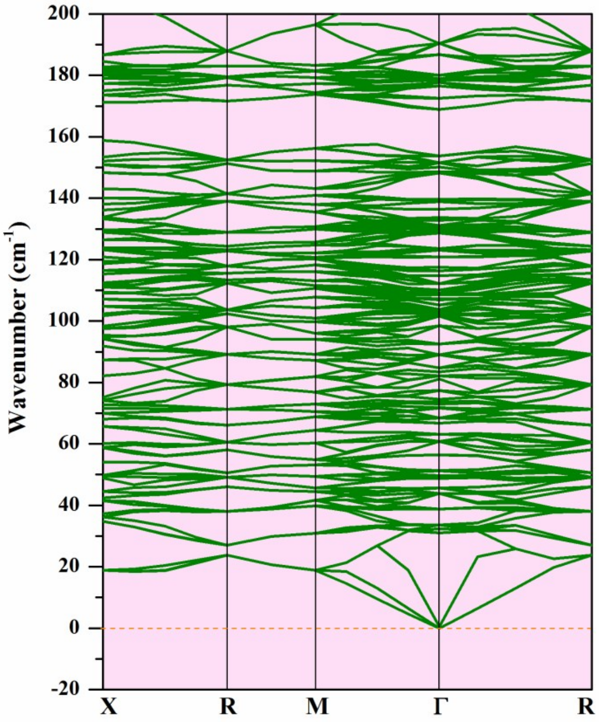

Figure S3. Calculated phonon dispersion of $K_6Cd_3(C_3N_3O_3)_4$.

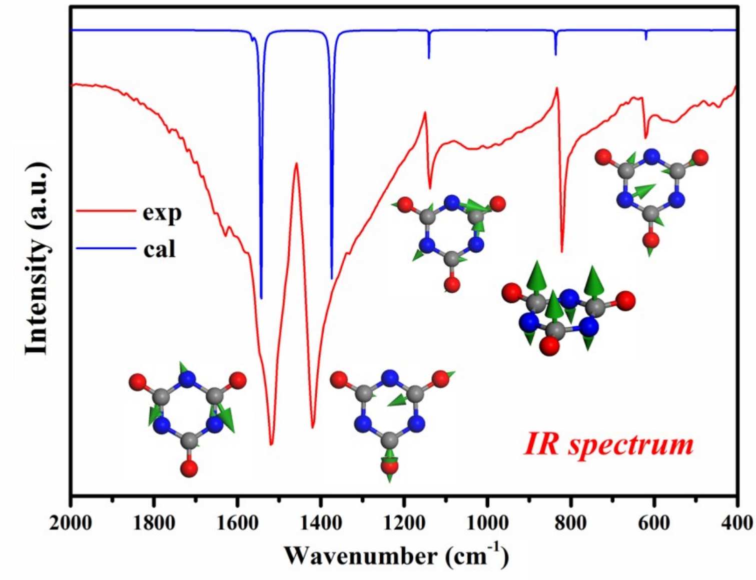

Figure S4. Experimental and simulated infrared spectra of $K_6Cd_3(C_3N_3O_3)_4$. The peaks locating at 1417 cm^{-1}, 1518 cm^{-1}, 1138 cm^{-1}, 821 cm^{-1} and 621 cm^{-1} are assigned to the corresponding vibrational modes by CASTEP.

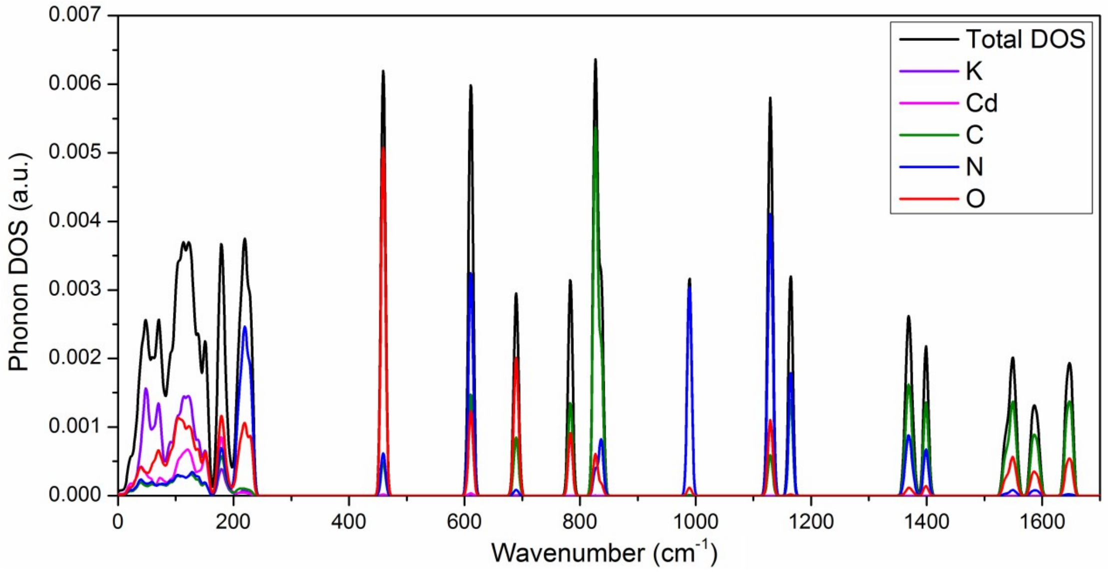

Figure S5. Total and partial density of phonon states of $K_6Cd_3(C_3N_3O_3)_4$.

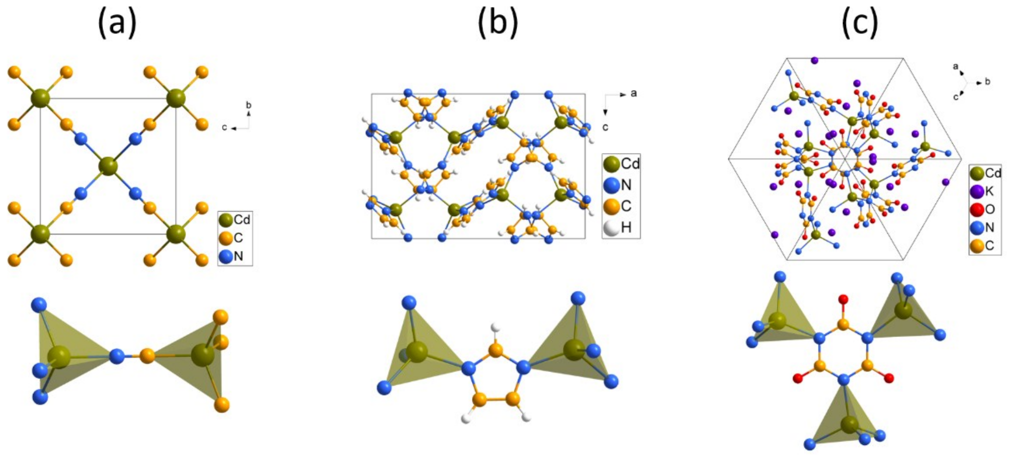

Figure S6. Structural comparisons between (a) $Cd(CN)_2$, (b) $Cd(H_3C_3N_2)_2$ and (c) $K_6Cd_3(C_3N_3O_3)_4$.

Table S1. The refined lattice constants and volumes of $K_6Cd_3(C_3N_3O_3)_4$ at various temperatures.

Temperature (K)	a (Å)	a/a_0 (10 K)	V (Å^3)	V/V_0 (10 K)
300	13.4104	1.00154	2411.712	1.00464
250	13.40352	1.00103	2408.003	1.00309
200	13.39611	1.00048	2404.011	1.00143
150	13.39126	1.00011	2401.398	1.00034
130	13.38983	1.00001	2400.629	1.00002
110	13.38942	0.99998	2400.407	0.99993
90	13.38961	0.99999	2400.509	0.99997
70	13.38939	0.99997	2400.391	0.99992
50	13.38961	0.99999	2400.509	0.99997
30	13.38949	0.99998	2400.446	0.99995
10	13.38973	1	2400.577	1

References

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