Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Intrinsic Volumetric Negative Thermal Expansion in the "Rigid" Calcium Squarate

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Experimental Section

Synthesis of Ca_sq.

A solution of squaric acid (228 mg, 2 mmol) and NaOH (160 mg. 4 mmol) in 20 mL deionized water was carefully layered onto a solution of $Ca(CH_3COO)_2{\cdot}H_2O$ (1.76 g, 10 mmol), $NaCH_3COO$ (5.44 g, 40 mmol), acetic acid (1.14 mL) in 50 mL deionized water. Colorless needle shaped single crystals began to appear after several days. The product was filtered, washed with deionized water and ethanol several times, and then dried at 350 K. Additionally, to meet the stand of synchrotron X-ray powder diffraction and pair distribution function (PDF) measurements, powder Ca_sq sample with smaller grain size was synthesized by sufficiently stirring the above solution for 12h.

Characterization

Thermogravimetric Analyses (TGA) measurement was performed using Mettler-Toledo instrument with a heating rate 5 K/min under air.

The high resolution synchrotron based X-ray powder diffraction (HR-SXRD) data were collected at the beamline BL02B2 of Spring-8 (Japan). The sample was fully grinded and activated at 500 K, then it was loaded into a 0.5 mm capillary and sealed in air. The wavelength was calibrated to λ = 0.77487 Å using a CeO_2 standard. The data were collected from 100 to 450 K with an interval of 25 K and the heating rate was 50 K min^{-1}. A series of *in situ* data were analyzed by Rietveld refinement using *Fullprof* program.[1, 2] The background, scale factor, lattice parameter, and zero point were refined. The Pseudo-voigt function was chosen to generate the peak shapes. The coordinates and temperature factor were also refined. The results are shown in Figure S3.

Single crystal X-ray diffraction (SCXRD) data was collected using a SuperNova diffractometer equipped with mirror Cu-K_α radiation (λ = 1.54184 Å). The structure was solved by the direct method using the SHEXLTL package and refined by the full-matrix least-squares method with SHELXTL.[3]

The pair distribution function (PDF) data was extracted from high energy synchrotron X-ray scattering by direct Fourier transform of reduced structure function (F(Q), up to Q = 22 Å) using the 11-ID-C beamline at Advanced Photon Source (APS) of Argonne National Laboratory.

The Raman spectrum was recorded using a multichannel modular triple Raman system (JY-HR800) with confocal microscopy. The solid-state diode laser (532 nm) from Coherent Company-Verdi-2 was used as an excitation source. Owing to the detector cut-off, the spectrum was collected from 50 to 2000 cm^{-1}. The DFT calculations were performed using the CASTEP program.[4] Before the vibration calculation, the crystal structure was fully optimized. The vibrational property was calculated by linear response formalism, in which the phonon frequencies were obtained by the second derivative of the total energy with respect to the given perturbation.

Table S1 Crystallographic data for Ca_sq·H_2O

Complex	**Ca_sq·H_2O**
Empirical formula	$C_4H_4CaO_6$
Formula weight	188
Temperature/K	300
Crystal system	Tetragonal
Space group	*I*−42*d*
a/Å	13.6309(3)
b/Å	13.6309(3)
c/Å	7.6942(5)
α/°	90
β/°	90
γ/°	90
Volume/$Å^3$	1429.59(11)
Z	8
D (g/cm^3)	1.766
μ/mm^{-1}	2.054
F(000)	770
Goodness-of-fit on F^2	1.260
Final R indexes [I>=2σ (I)]	R_1 = 0.0257, wR_2 = 0.0818
Final R indexes [all data]	R_1 = 0.0261, wR_2 = 0.0820

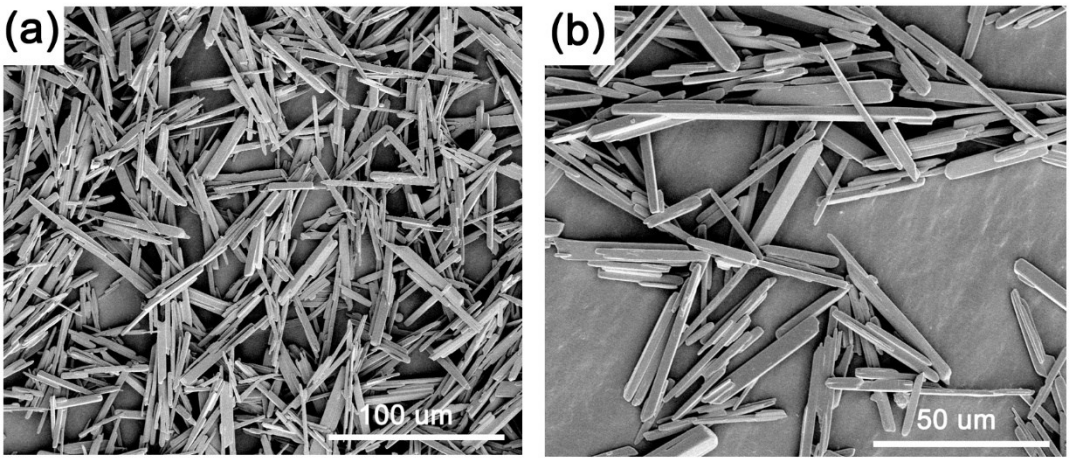

Figure S1. SEM images of Ca_sq with the magnification x500 (a) and x1000 (b).

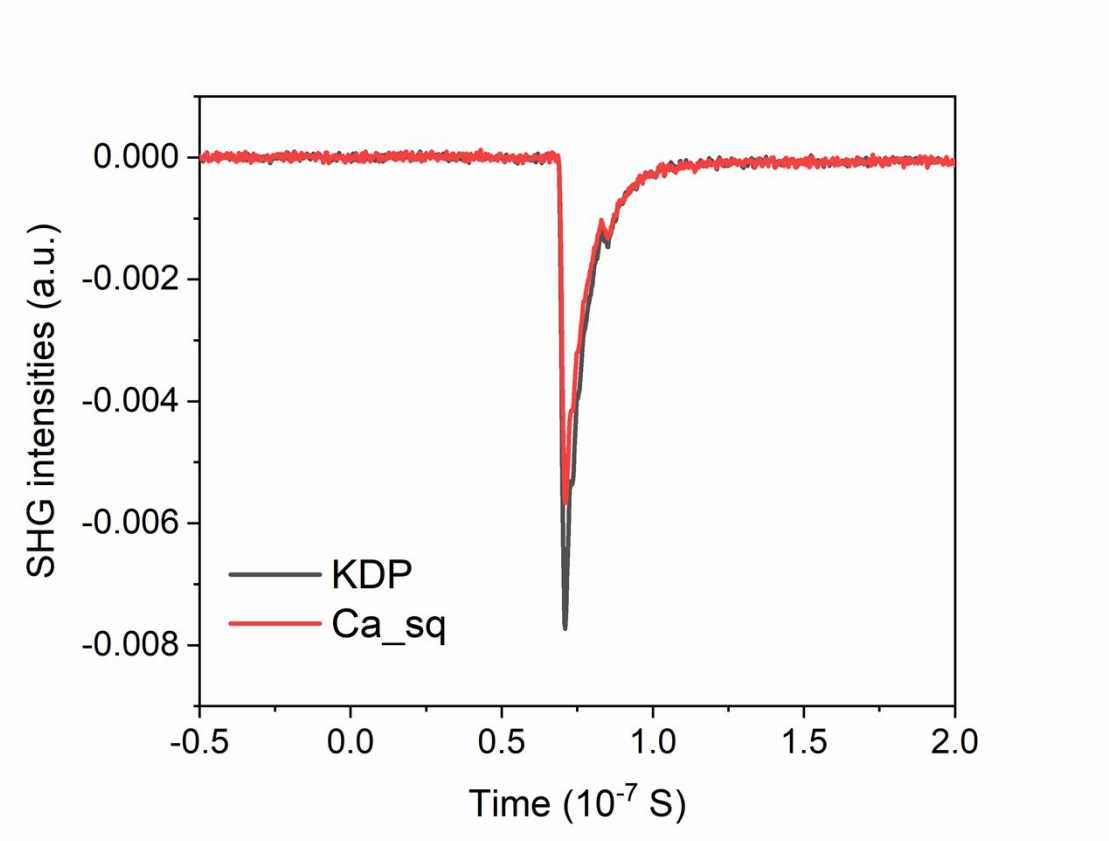

Figure S2 Oscilloscope traces of the SHG signal of Ca_sq compared with KH_2PO_4 (KDP).

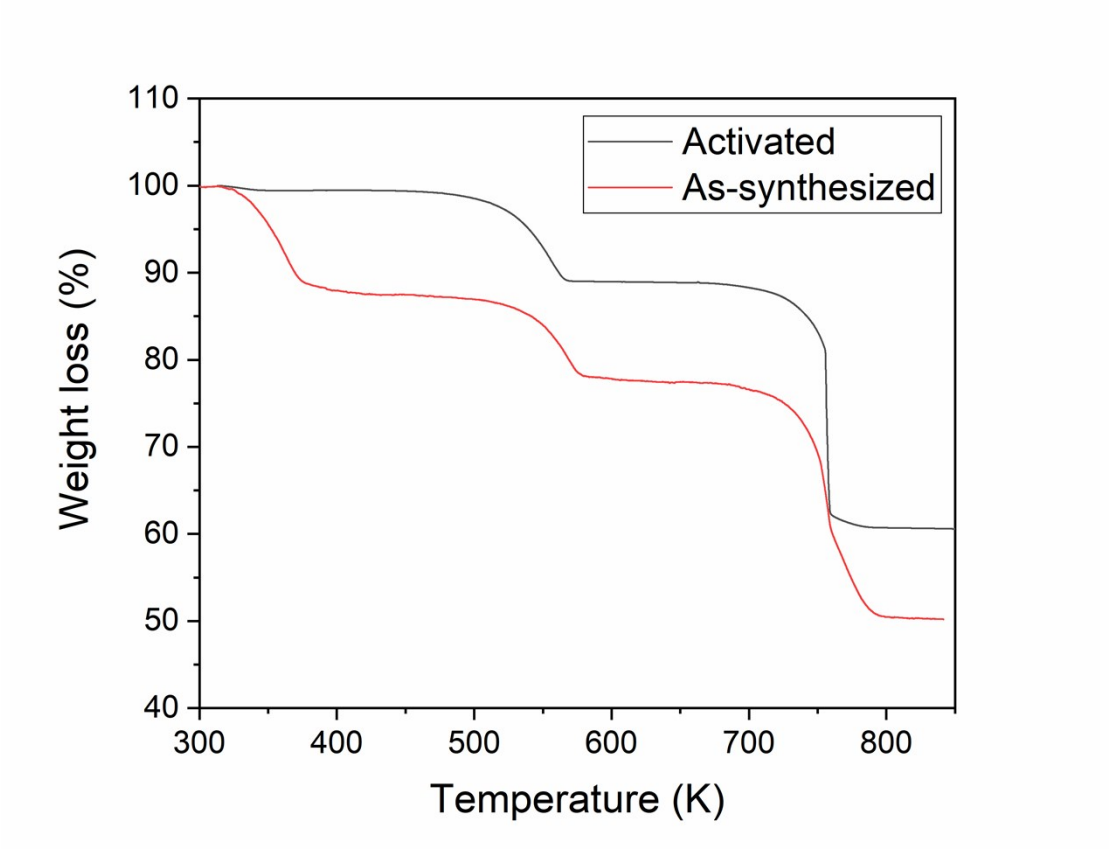

Figure S3 TGA of the as-synthesized (red) and activated (black) Ca_sq under air.

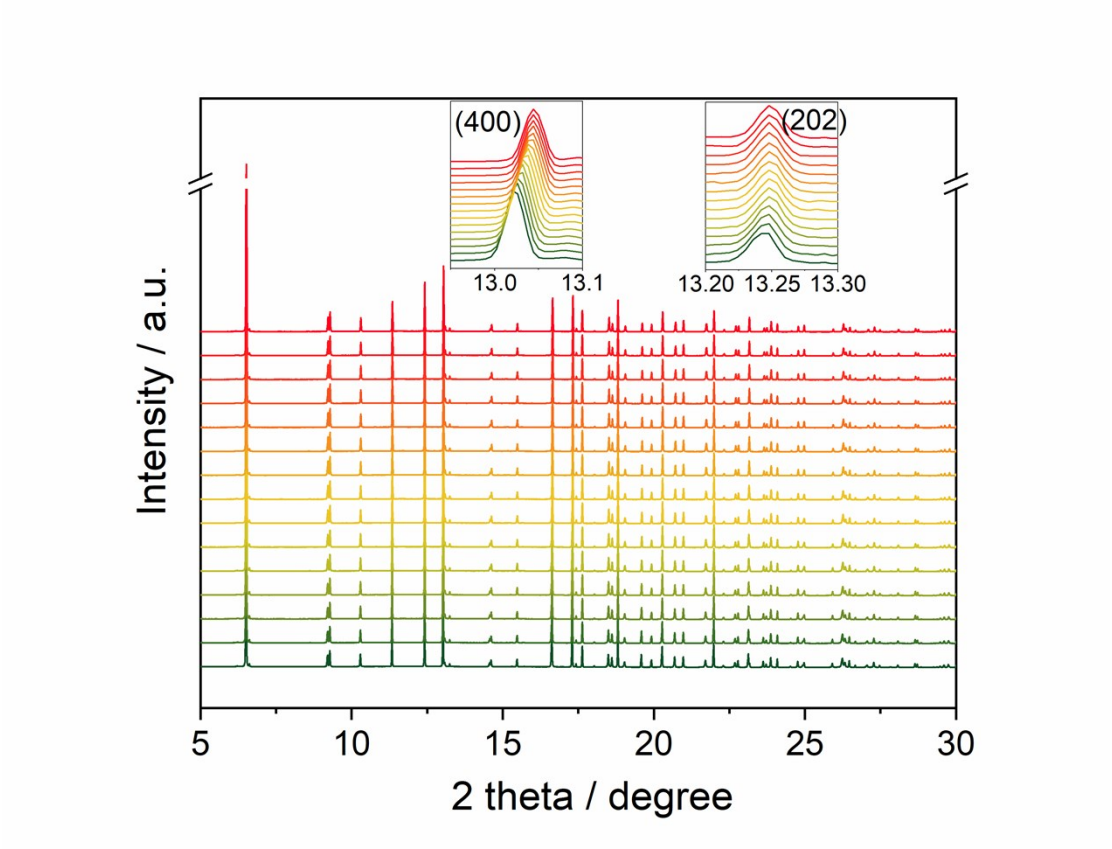

Figure S4 Temperature dependent HR-SXRD patterns of the activated Ca_sq. The insets show the zoomed peak shifts of (400) (left) and (202) (right)

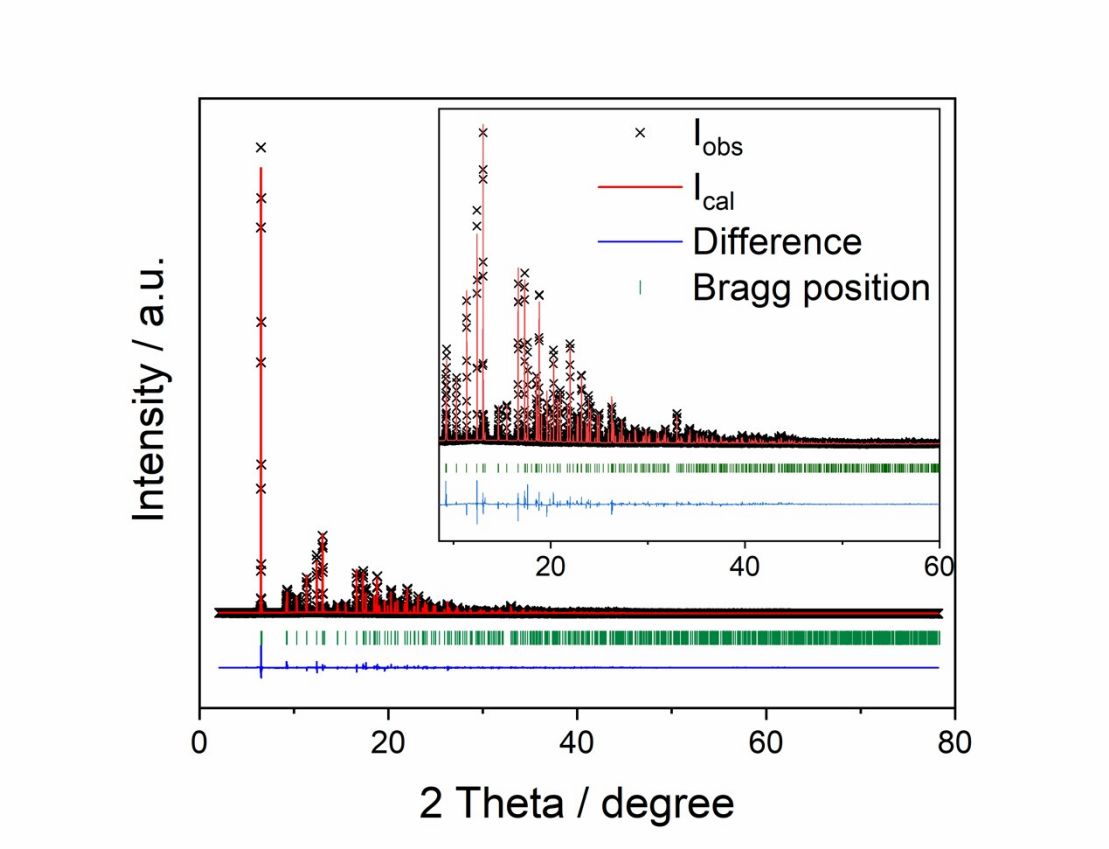

Figure S5 Rietveld refinement pattern of Ca_sq at 300 K, the inset shows the zoomed pattern at higher angels (R_{wp} = 8.6%, R_p = 6.14%).

Table S2 The lattice parameters extracted from the Rietveld refinement results based on the HR-SXRD data.

Temperature	*a* (Å)	*c* (Å)	*V* (Å^3)
100	13.67506(6)	7.72188(4)	1444.049(12)
125	13.67239(6)	7.72104(4)	1443.327(12)
150	13.66993(6)	7.72050(4)	1442.707(12)
175	13.66783(6)	7.72020(4)	1442.207(11)
200	13.6658(6)	7.72015(4)	1441.769(11)
225	13.66362(6)	7.72031(4)	1441.340(11)
250	13.66139(6)	7.72057(3)	1440.916(11)
275	13.65927(6)	7.72088(3)	1440.528(11)

300	13.65741(6)	7.72117(3)	1440.191(11)
325	13.65592(6)	7.72139(3)	1439.916(10)
350	13.65480(6)	7.72157(3)	1439.712(10)
375	13.65387(6)	7.72175(3)	1439.550(11)
400	13.65327(6)	7.72180(3)	1439.434(11)
425	13.65287(6)	7.72163(3)	1439.319(11)
450	13.65253(6)	7.72161(3)	1439.243(11)

Table S3 Some representative ZTE compounds and their coefficients.

Compound Name	Linear CTE ($\times 10^{-6}$ K^{-1})	Temperature range	Reference
$N(CH_3)CuZn(CH_3)_4$	+0.2	200~400K	5
$(Sc_{0.85}Ga_{0.05}Fe_{0.10})F_3$	+0.23	300~900K	6
$Mn_3Cu_{0.5}Ga_{0.5}N$ (ultrananocrystalline)	+0.12	12~230K	7
$Tb(Co_{1.9}Fe_{0.1})$	+0.48	13~307	8
$ZrMgMo_3O_{12}$	+0.16	298~723K	9
$[Cd(HBTC)(BPP)]\cdot 1.5DMF\cdot 2H_2O$	+2	100~260K	10
Ba_sq	-2.2	125~550K	11
Pb_sq	-0.61	125~550K	
$(C_3H_5N_2)_2K[Co(CN)_6]$	+1.7	200~300K	12
$(C_3H_5N_2)_2K[Fe(CN)_6]$	-1.3	200~300K	
Ca_sq	-0.14	100~450K	This work

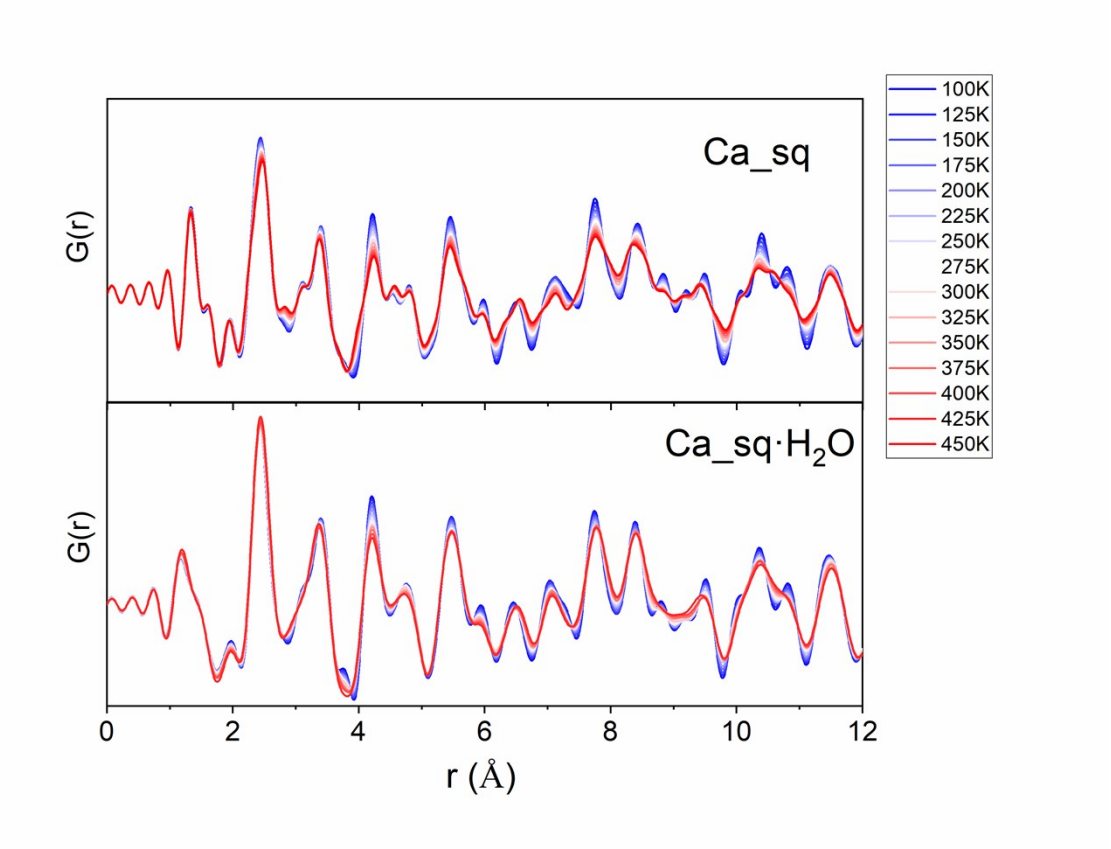

Figure S6 Temperature dependent PDF patterns of the as-synthesized (bottom) and activated Ca_sq (top). The data for the as-synthesized and activated sample was recorded from 100 to 350 K and 100 to 450 K, respectively.

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