

Pressure and Temperature Phase Diagram of CsCaCl₃

SUPPLEMENTARY INFORMATION

Craig L Bull,^{a,b} Christopher J Ridley,^a Nicholas Funnell,^a Sumit Komar,^b and James Cumby^b

^a ISIS Facility, Rutherford Appleton Laboratory, Harwell Science and Innovation Campus,
Didcot, OX11 0QX, UK

^b EastCHEM School of Chemistry, Joseph Black Building, David Brewster Road, Edinburgh, EH9 3FJ, UK

*To whom correspondence should be addressed;

E-mail: craig.bull@stfc.ac.uk

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Table S1: Derived structural parameters for a perovskite in both cubic ($P\bar{3}m$) and tetragonal ($I4/mcm$) symmetry, where ($\tan(\phi) = 4u$) and u is the displacement of the x and y co-ordinate of the Cl atom in the tetragonal phase (after K. S. Knight *et al*, Physics and Chemistry of Minerals 41, 461 (2014))

| Structural Parameter | $Pm\bar{3}m$ | $I4/mcm$ |
|------------------------|----------------------|---|
| A-X(1) | $\frac{a}{\sqrt{2}}$ | $\frac{a}{2}$ |
| A-X(2) | - | $\frac{1}{4} [2a^2 (1 - 2\phi + \phi^2 - \frac{2}{3}\phi^3) + c^2]^{0.5}$ |
| A-X(2) | - | $\frac{1}{4} [2a^2 (1 + 2\phi + \phi^2 + \frac{2}{3}\phi^3) + c^2]^{0.5}$ |
| B-X(1) | $\frac{a}{2}$ | $\frac{c}{4}$ |
| B-X(2) | - | $\frac{a}{2\sqrt{2}} [1 + \frac{1}{2}\phi^2 + \frac{5}{24}\phi^4]$ |
| AX _n volume | $\frac{5a^3}{6}$ | $\frac{a^2c}{24} [3 - \phi - \frac{1}{3}\phi^2 - \frac{2}{15}\phi^5 - \frac{17}{315}\phi^7]$ |
| BX ₆ volume | $\frac{a^3}{6}$ | $\frac{a^2c}{24} [1 + \phi^2 + \frac{2}{3}\phi^4 + \frac{17}{45}\phi^6 + \frac{62}{315}\phi^8]$ |

$$l_{pc}(T) = l_{pc0} + \frac{A_{pc}}{\exp\left(\frac{B_{pc}}{T}\right) - 1}$$

Einstein internal energy model fitted to the pseudo-cubic lattice parameter l_{pc} with temperature (T) using an Einstein temperature (B_{pc}). For these models we find $a_{pc0}=5.3650 \text{ \AA}$, $A_{pc}=0.0466 \text{ \AA}$, $B_{pc}=129.5 \text{ K}$ and $c_{pc0}=5.3981 \text{ \AA}$, $A_{c_{pc}}=-0.0431 \text{ \AA}$, $B_{c_{pc}}=140.7 \text{ K}$.

$$e_a = (2e_1 + e_3)$$

$$e_{tz} = \frac{2}{\sqrt{3}}(e_3 - e_1)$$

$$e_1 = \frac{a/\sqrt{2} - a_0}{a_0}$$

$$e_3 = \frac{c/2 - a_0}{a_0}$$

Equations for the symmetry-adapted tetragonal strain, e_{tz} , volumetric strain, e_a , and natural linear strain components e_1 and e_3 . a_0 is calculated from the pseudo cubic unit-cell volume of the tetragonal phase ($\sqrt{[3]a_{pc}^2c_{pc}}$) at each temperature. As $e_1 < 0$, $e_3 > 0$ and $e_3 \simeq 2|e_1|$, by definition $e_a = 0$ and $e_{tz} > 0$.

$$\cos(\alpha_{pc}) - \cos(\alpha_{pc})_{calc} = \left(\frac{2}{3}\right) \zeta \left[1 - \left(\frac{2}{3}\right) \sin^2\omega\right]^{-1}$$

$$\cos(\alpha_{pc})_{calc} = \frac{\sin^2\omega}{3 - 2\sin^2\omega}$$

Formulation for the octahedral strain ζ (equal to 0 in the undistorted, cubic phase). ω is the octahedral tilt angle in the rhombohedral phase.

$$V(T) = V_0 + \frac{9N\gamma_1 k_B z T}{B_0} \left(\frac{T}{\Theta_{D1}}\right)^3 \int_0^{\frac{\Theta_{D1}}{T}} \frac{x^3 dx}{e^x - 1} + \frac{9N\gamma_2 k_B (1-z) T}{B_0} \left(\frac{T}{\Theta_{D2}}\right)^3 \int_0^{\frac{\Theta_{D2}}{T}} \frac{x^3 dx}{e^x - 1}$$

$$c_V(T) = 9Nk_B z \left(\frac{T}{\Theta_{D1}}\right)^3 \int_0^{\frac{\Theta_{D1}}{T}} \frac{x^4 e^x dx}{(e^x - 1)^2} + 9Nk_B (1-z) \left(\frac{T}{\Theta_{D2}}\right)^3 \int_0^{\frac{\Theta_{D2}}{T}} \frac{x^4 e^x dx}{(e^x - 1)^2}$$

Formulation of unit-cell volume and isochoric heat capacity as a function of temperature according to the two-term Debye approximation. V_0 is the unit-cell volume at zero temperature, N is the number of atoms, γ_n are the Grüneisen parameters, k_B is the Boltzmann constant, B_0 is the isothermal bulk modulus, z is the mixing coefficient for the two-term model, and θ_{Dn} are the Debye temperatures. In the present study the fitting was performed using the GlobalAnalysis package in IgorPro (©WaveMetrics), allowing for the global minimisation of both integrals against two physical datasets with shared fitting parameters.

$$M_i = \left(\frac{R_i N_i}{B}\right) \exp\left[\left(\frac{R_0 - R_i}{B}\right)\right]$$

Formulation of M_i , the total estimated variation of bond valence in a polyhedral site due to the change of average bond distance. R_i is the average measured bond distance in the polyhedra, N_i is the coordination number in the polyhedra, R_0 is a constant for a particular atom pair and B is a universal constant (0.37), the values of which are given and defined in the work of Brown and Altermatt (Acta Cryst. B41, 244-247 (1985)) The relative values of M for the A site (M_A) and (M_B) give an indication of the relative compressibilities (full derivation and description is given in Zhao *et al* Acta Cryst B 60, 3, 263-272 (2004). For $M_A/M_B \geq 1$ the material will become more symmetric upon compression, $M_A/M_B \approx 1$ the distortion does not change with pressure and $M_A/M_B \leq 1$ indicates that the distortion will increase with increasing pressure.

Table S2: Determined structural parameters of CsCaCl₃ with temperature. For the tetragonal structure the space-group is $I4/mcm$, Cs $4b$, Ca $4c$, Cl(1) $4a$, Cl(2) $8h \frac{1}{4}+u, \frac{3}{4}+u, 0$. For $Pm\bar{3}m$; Wyckoff positions: Cs $1b$, Ca $1a$, Cl $3d$ For further details see main text

| Temperature (K) | Phase | a(Å) | c(Å) | V(Å ³) | u |
|-----------------|------------|-----------|-------------|--------------------|---------|
| 5 | Tetragonal | 7.7880(3) | 10.7952(5) | 621.57(7) | 0.0233 |
| 25 | Tetragonal | 7.5864(3) | 10.7968(5) | 621.40(7) | 0.02387 |
| 45 | Tetragonal | 7.5920(3) | 10.7923(5) | 622.06(7) | 0.02197 |
| 65 | Tetragonal | 7.5970(3) | 10.7846(6) | 622.42(7) | 0.0193 |
| 70 | Tetragonal | 7.6998(3) | 10.7825(6) | 622.77(6) | 0.01777 |
| 80 | Tetragonal | 7.6033(4) | 10.7787(8) | 623.12(6) | 0.01595 |
| 90 | Tetragonal | 7.6079(6) | 10.7732(10) | 623.56(6) | 0.01323 |
| 100 | Cubic | 5.3836(2) | - | 156.030(14) | - |
| 120 | Cubic | 5.3848(2) | - | 156.138(15) | - |
| 140 | Cubic | 5.3869(2) | - | 156.323(17) | - |
| 160 | Cubic | 5.3888(2) | - | 156.49(2) | - |
| 180 | Cubic | 5.3902(2) | - | 156.61(2) | - |
| 200 | Cubic | 5.3923(3) | - | 156.79(2) | - |
| 220 | Cubic | 5.3941(3) | - | 156.95(3) | - |
| 240 | Cubic | 5.3962(3) | - | 157.13(3) | - |
| 260 | Cubic | 5.3991(3) | - | 157.38(3) | - |
| 280 | Cubic | 5.4004(3) | - | 157.50(3) | - |

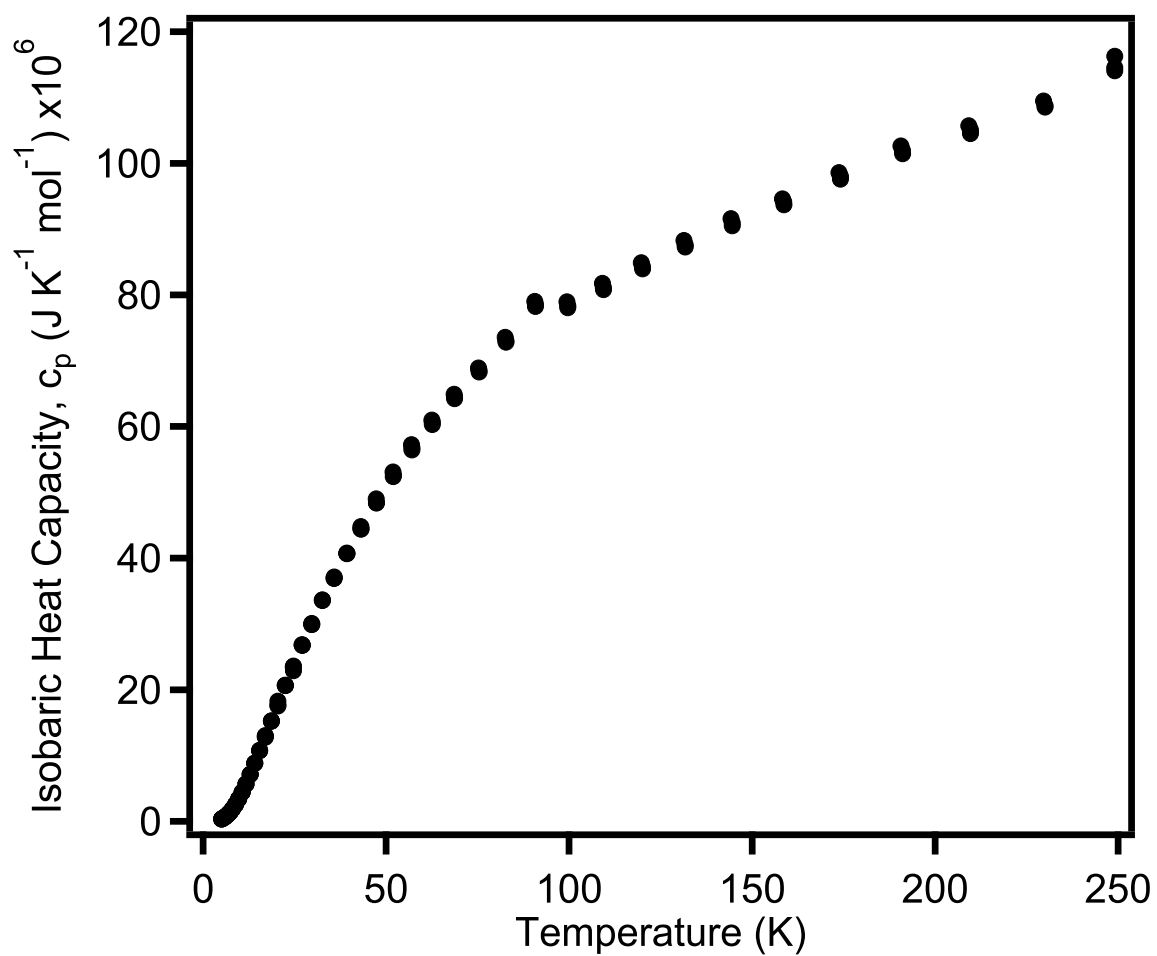


Figure S1: Isobaric heat capacity as a function of temperature, collected on warming from 4 K. There is a clear discontinuity at the expected transition temperature between 90 and 100 K.