Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting information for: A general forcefield for accurate phonon properties of metal-organic frameworks

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Method integration

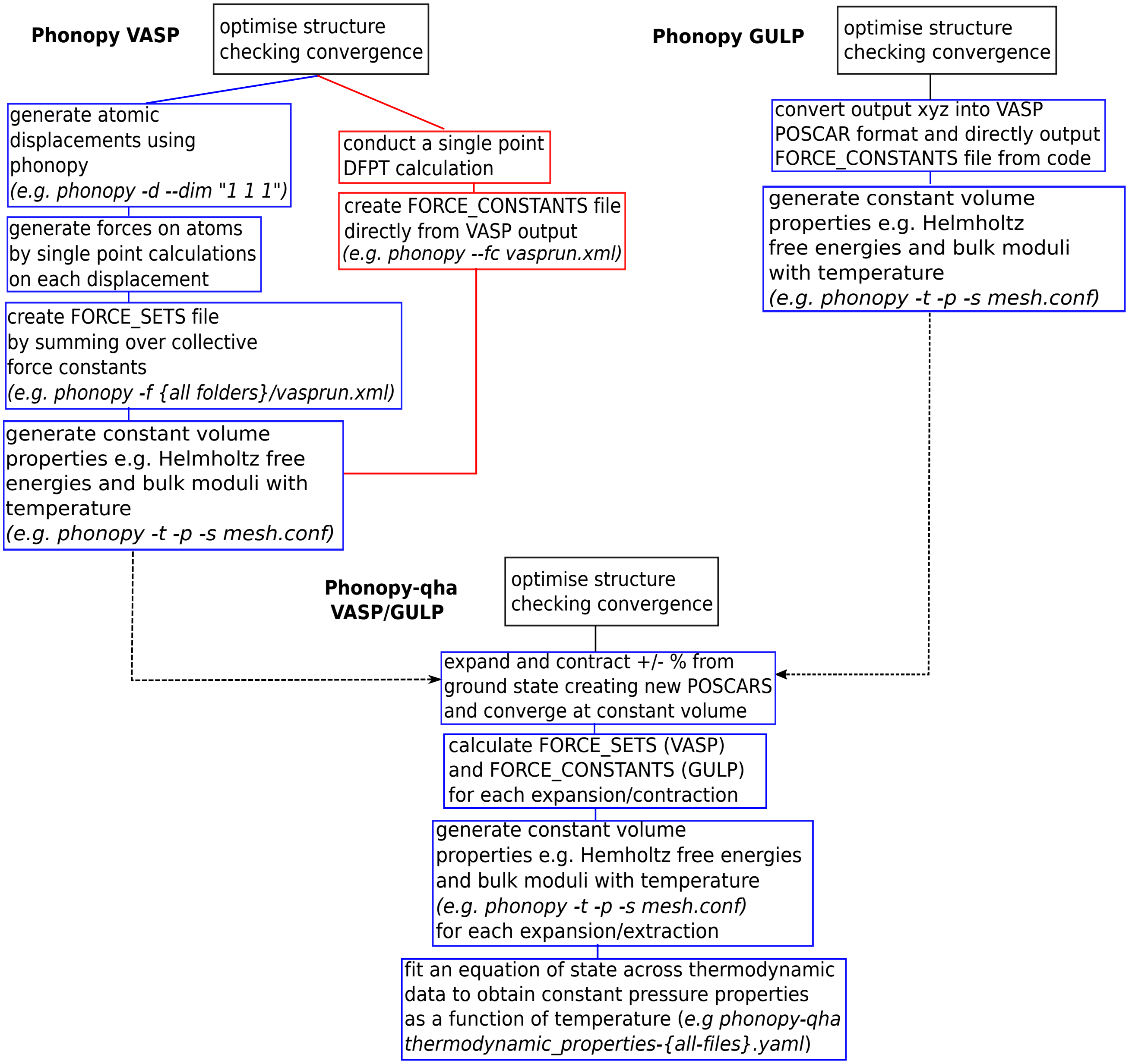

Figure S1: The integration process of using Phonopy, VASP and GULP for the calculation of thermodynamic properties.

Phonon property calculation

Following optimisation of the structures the vibrational frequencies are calculated as the square root of the eigen values of the mass weighted dynamical matrix. Once the vibrational frequencies have been calculated a range of thermodynamic properties can be calculated. The quasi-harmonic approximation introduces volume dependence of phonon frequencies as a function of temperature allowing the Gibbs free energy to be calculated as given by:

Gibbs free energy (G) under the quasi-harmonic approximation:

$\mathrm{G(T,p)} = \mathrm{min}_V\ [\mathrm{U(V)} + \mathrm{A}_{phonon}(\mathrm{T;\ V}) + \mathrm{pV}]$

where, min_V is a unique minimum of the Helmholtz vibrational free energy (A) as a function of temperature (T) and pressure (p) and U is the internal energy.

Here we summarise each property calculated from the quasi-harmonic approximation:

Bulk modulus ($\mathbf{B}_0$):

The bulk modulus is a measure of the mechanical strength of a material and describes the resistivity of a structure to compression as given by:

$$B_0 = -V\left(\frac{\delta p}{\delta V}\right) \tag{1}$$

Specific heat capacity (constant pressure) ($\mathbf{C}_p$):

The heat capacity describes the ability of a material to store internal energy at a given temperature and reflects the phonon occupation of vibrational levels. Once all levels are saturated, the specific heat capacity at both constant pressure (C_p) and volume (C_v) reach a thermodynamic limit and a plateau is observed that corresponds to the Dulong-Petite limit ($\frac{3}{2}$ k_B per atom).

$$\left(\frac{\delta U}{\delta T}\right)_v = \left(\frac{\delta Q}{\delta T}\right)_v \tag{2}$$

$$\left(\frac{\delta H}{\delta T}\right)_p = \left(\frac{\delta Q}{\delta T}\right)_p \tag{3}$$

where, H the enthalpy of the system and Q is heat.

Gr$\ddot{u}$neisen parameter:

The definition of the Grüneisen parameter (γ) in terms of volume dependence of the *ith* vibrational mode (ω_i):

$$\gamma_i = -\frac{\delta ln\omega_i}{\delta lnV} \tag{4}$$

When summing all γ_i through the first Brillouin zone the thermodynamic definition of the Grüneisen parameter becomes:

$$\gamma_{th} = \frac{\alpha V B_0}{C_v} \tag{5}$$

where, α is the volumetric thermal expansion, B_0 the isothermal bulk modulus and C_v is the heat capacity at constant volume.[S1]

The Grüneisen parameter is a thermodynamic description of the change in frequency of each vibrational mode with change in volume. When plotted against temperature, a negative Grüneisen parameter corresponds to a soft (low frequency) vibrational mode.

Volumetric thermal expansion (α_V):

The volumetric thermal expansion coefficient described the change in volume of unit cell as a function of temperature.

$$\alpha_v = \frac{1}{V}\left(\frac{\delta V}{\delta T}\right)_p \tag{6}$$

DFT convergence for metal oxides

Table S1: Converged **k**-point grid and plane wave cut-off values used for reference metal oxides. Unit cell parameters are given for DFT (above) and VMOF (below).

Metal oxide	**k**-point grid	Plane wave cut-off	unit-cell parameters (**a b c**, α β γ)	space group
ZnO	10 × 10 × 10	600	3.225 3.225 5.211, 90 90 120	186
			3.166 3.166 4.943, 90 90 120	
ZrO_2	12 × 12 × 12	700	5.064 5.064 5.064, 90 99 90	14
			5.123 5.123 5.123, 90 90 90	
TiO_2	10 × 10 × 10	600	4.585 4.585 2.941, 90 90 90	136
			4.414 4.414 3.168, 90 90 90	
Al_2O_3	8 × 8 × 6	700	4.755 4.755 12.962, 90 90 120	167
			4.870 4.870 12.899, 90 90 120	

Metal oxide forcefield fitting

A modification of the universal MM3 Buckingham constants was found to be beneficial to the second order properties of the metal oxides used for parameterising some metal-oxygen interactions in the frameworks. Table S2 gives the structural and mechanical properties calculated prior to the modification using the original MM3 Buckingham constants.

Table S2: Comparison of mechanical and structural properties of metal oxides between experiment (Exp) and forcefield (FF) using MM3 constants that have not been modified following a relaxed fitting procedure.

	ZnO		ZrO_2		TiO_2		Al_2O_3	
Property	Exp[S2]	FF	Exp[S3]	FF	Exp[S4]	FF	Exp[S5]	FF
C_{11} (GPa)	209.6	305.3	533.5	800.6	366.0	448.7	497.3	665.0
C_{12} (GPa)	121.1	123.6	97.86	148.1	225.0	411.1	162.8	294.6
C_{13} (GPa)	105.1	115.3	-	-	-	-	116.0	171.1
C_{33} (GPa)	210.9	199.2	-	-	-	-	500.9	589.3
C_{44} (GPa)	-	-	64.26	132.4	189.0	267.6	146.8	127.8
C_{55} (GPa)	42.5	103.0	-	-	-	-	-	-
B_0 (GPa)	183.0	175.4	243.7	365.6	282.0	411.5	240.0	351.7
a (Å)	3.250	2.994	5.070	4.794	4.594	4.125	4.764	4.533
b (Å)	3.250	2.994	5.070	4.794	4.594	4.125	4.764	4.533
c (Å)	5.207	4.680	5.070	4.794	2.959	2.967	13.001	12.062
M-O (Å)	1.992	1.799, 1.841	2.195	2.076	1.980, 1.949	1.804, 1.854	1.858	1.697

Phonon dispersion curves

The phonon dispersion curves for ZnO and MOF-5 have been calculated using VMOF (Figure S2) along the appropriate symmetry paths.

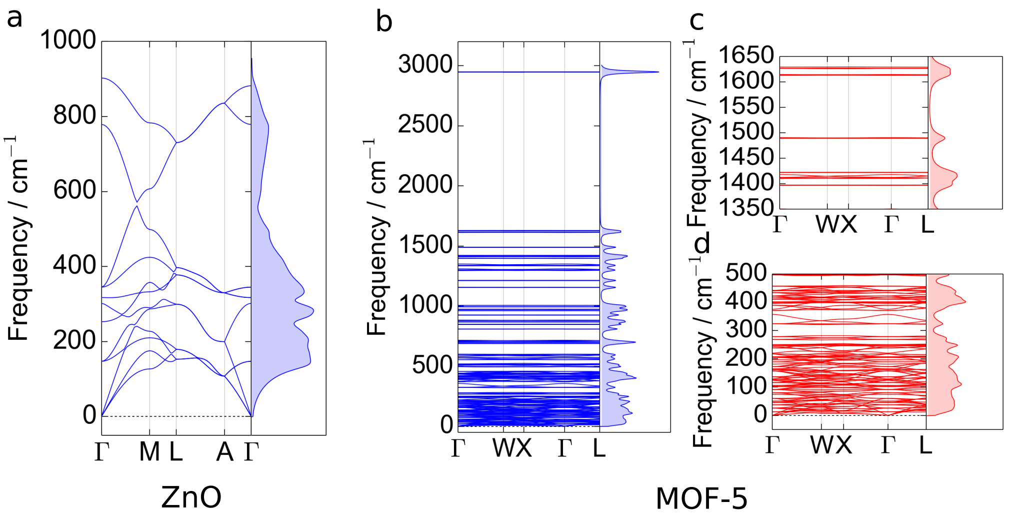

Figure S2: Phonon dispersion curves of a) ZnO (-50-1000 cm^{-1}), b) MOF-5 (-50-3000 cm^{-1}), c) MOF-5 (1350-1650 cm^{-1}), d) MOF-5 (-50-500 cm^{-1}). For all phonon dispersion curves the corresponding DOS are plotted (right).

A comparison of phonon dispersion curves of ZnO and MOF-5, show that due to the large system sizes of the MOFs studied in this paper, the plotted bands are predominately flat. Small dispersion can be observed between -50-500 cm^{-1} and 1350-1650 cm^{-1}. The vibrational modes corresponding to the dispersed bands are those of low energy ligand-metal node coupling of the ligand rocking (0-50 cm^{-1}) and rotating, vibrations within the metal node itself (50-500 cm^{-1}) and at the higher frequencies the modes correspond to the asymmetric and symmetric stretch of the carboxylate group coupled to the metal cations (1350-1650 cm^{-1}). When compared to the observed dispersion in ZnO (Figure S2a) the phonon dispersion curves give little additional vibrational information.

Clusters of MOF-5 for ligand rotation

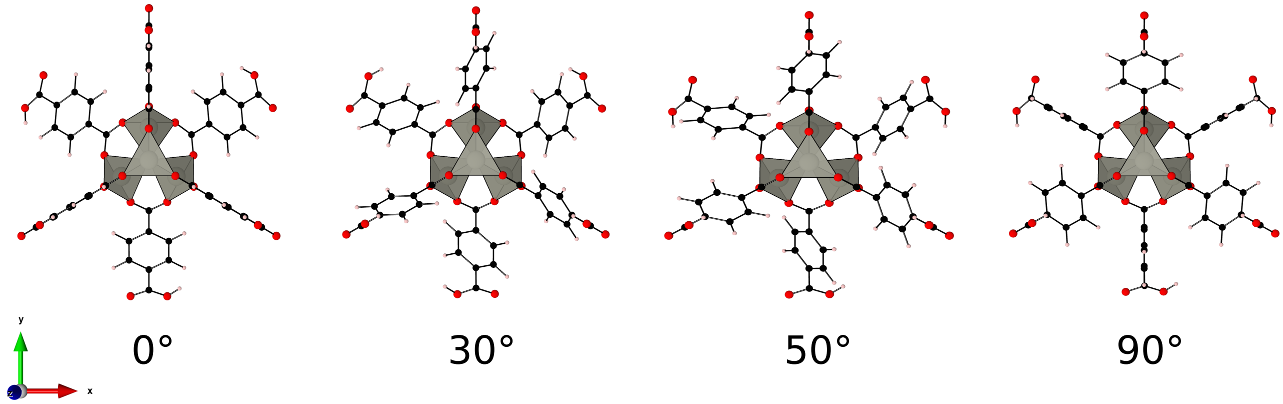

Figure S3: The protonated neutral clusters of MOF-5 used to model rotations of the BDC ligand using DFT and the PBE0 functional.

Quasi-harmonic parametrisation of IRMOF-10

IRMOF-10 was calculated to have multiple imaginary frequencies when compressed past 1.5 % away from the equilibrium volume. Results using the quasi-harmonic approximation are given for different compressions as described of the framework to analyse the sensitivity of the resultant thermodynamic properties of the different models.

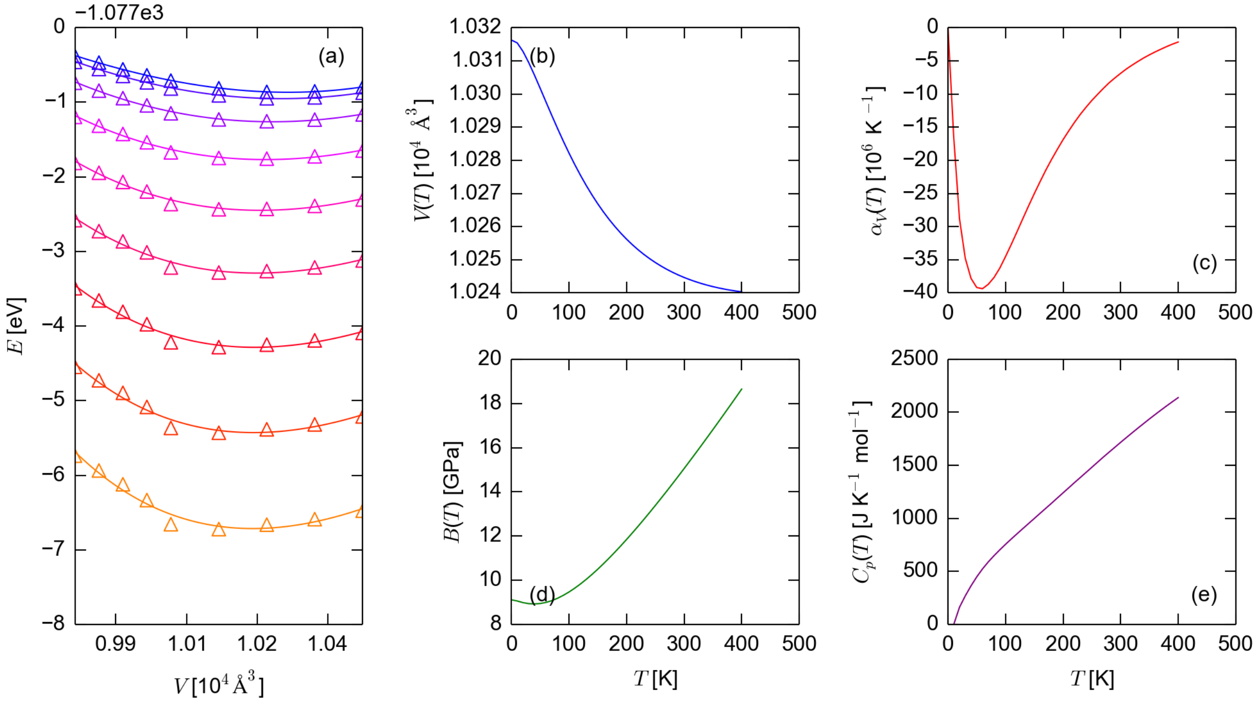

Figure S4: Quasi-harmonic equation of state fit and material properties with DFT for IRMOF-10 with +/-3% compression including all high pressure data points.

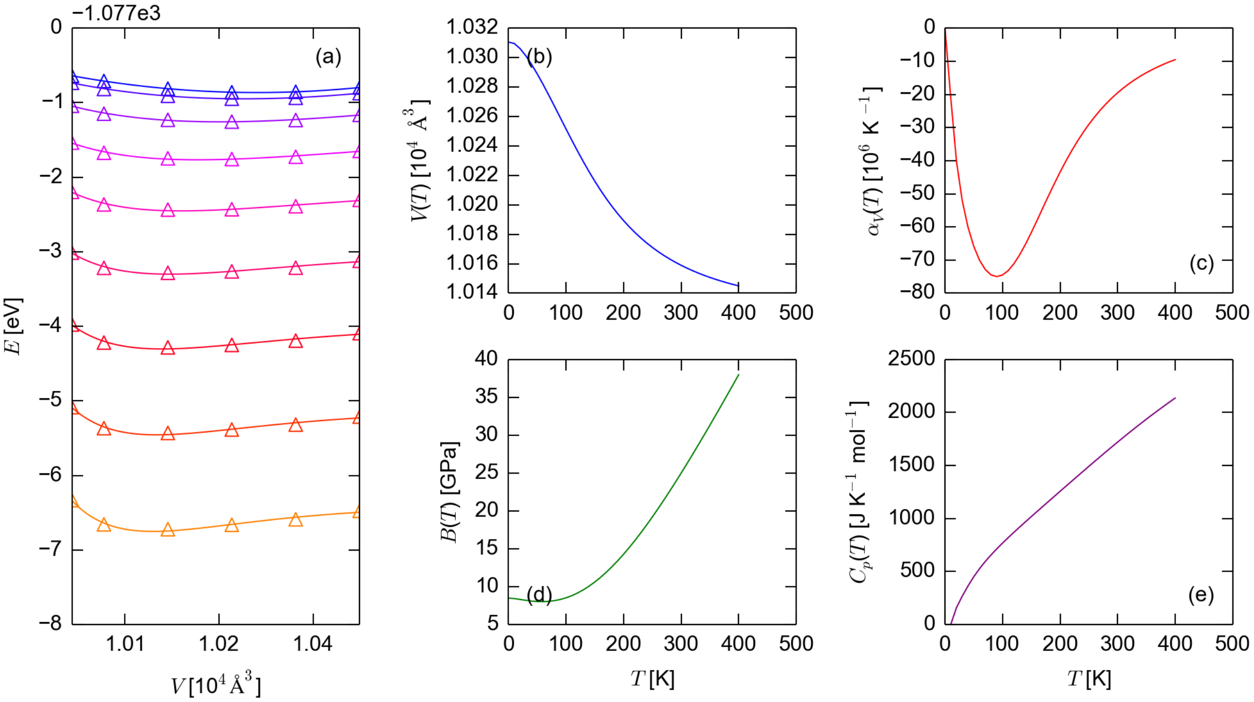

Figure S5: Quasi-harmonic equation of state fit and material properties with DFT for IRMOF-10 with +/-3% compression excluding highest pressure points.

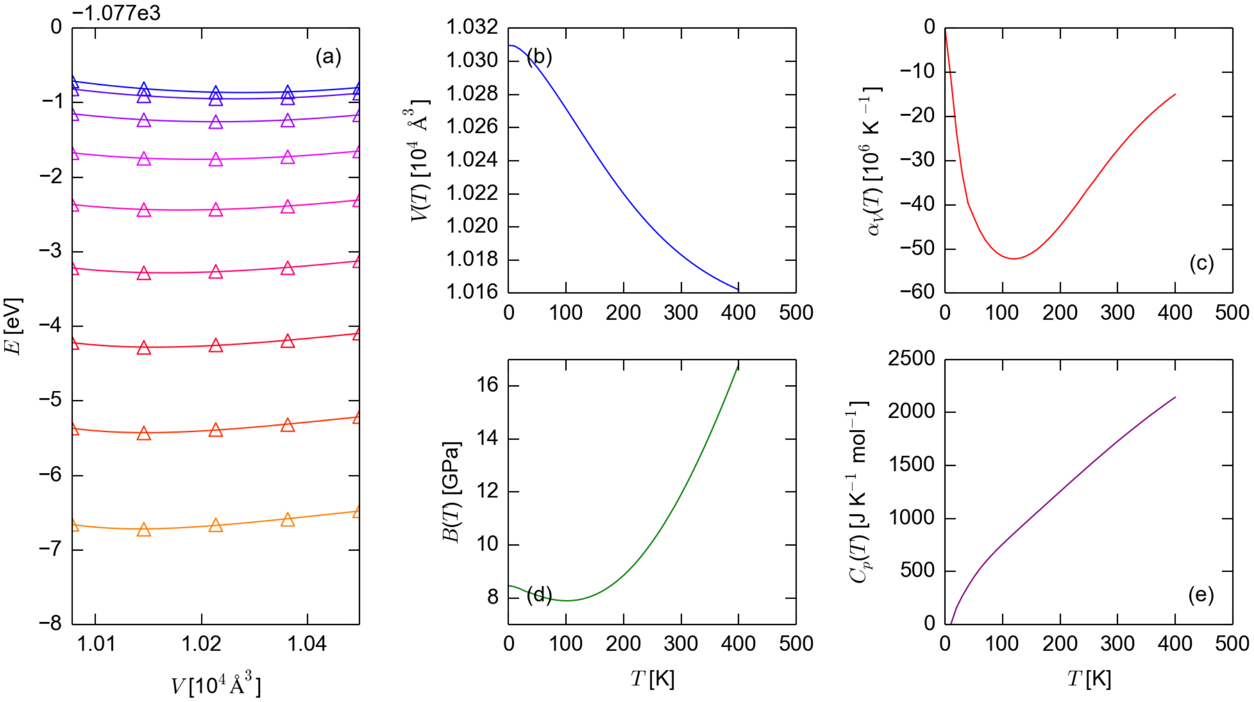

Figure S6: Quasi-harmonic equation of state fit and material properties with DFT for IRMOF-10 with +/-3% compression excluding all high pressure points.

References

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