Electronic Supplementary Information

Controllable Growth of Bulk Cubic-Phase $CH_3NH_3PbI_3$ Single Crystal with Exciting Room-Temperature Stability

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Experimental sections

Chemicals and reagents

Lead iodide (AR), lead bromide (AR) and lead chloride (AR) were purchased from Aladdin. Hydroiodic acid (≥45wt.% in water), hydrobromic acid (≥40 wt.% in water), hydrochloric acid(≥36 wt.% in water), methylamine (≥27 wt.% in methanol), DMF (AR), GBL (AR), DMSO (AR) and CB (AR) were purchased from Sinopharm Chemical Reagent Limited Corporation.

Preparation of Materials

Methylamine of 15 g was slowly added into hydroiodic acid solution of 30 g. The obtained solution was stirred in the ice bath for 2 hours. After reaction, the clean solution was evaporated at 60℃ for 2 h to obtain CH_3NH_3I salt. The white CH_3NH_3I sample was collected after dried in vacuum for 24 h at 70 °C. CH_3NH_3Br and CH_3NH_3Cl were synthesized in the similar processes.

To obtain $MAPbI_3$, CH_3NH_3I (3.95 g) and PbI_2 (11.57 g) were dissolved in GBL (20 mL) at room temperature for 3 h with stirring. Then 200 ml CB was added into the above solution with stirring and the black solids ($MAPbI_3$) was synthesized. The $MAPbI_3$ was collected by filtration, washing with CB, and then dried in vacuum for 24 h at 70 °C.

The saturated solubility of MAPbI3 was firstly investigated in GBL solution with excess MAPbI3by increasing temperature form 40 to 100 °C. The saturated solubility of $MAPbI_3$ was obtained by measuring the obtained perovskite of 0.5 g saturated solution drying at 100 °C for 0.5 hour. The saturated solubility was firstly investigated in mixed GBL and CB solution with different mass ratios (10 to 90% of GBL/ (GBL+CB)). More details are provided in Supporting Information.

Crystal growth

The growth solutions of single crystal $MAPbX_3$ were prepared with CB and a solution of $MAPbX_3$ (30 wt%), then heating at 60 °C temperature. A large number of small (~1–2 mm in size) crystal seeds were obtained once the above solution was heated and kept at 60 °C for overnight. For large crystal growth, only one seed was picked. By putting the seed into fresh solution, heated and kept it at 60 °C for 10–24 hours, the original crystal seed is found to grow into a larger (~4–6 mm) one. Repeating the above processes for 4 times, a larger crystal was formed with the size of 15 mm × 15 mm × 10 mm. Orange $CH_3NH_3PbBr_3$ and clear $CH_3NH_3PbCl_3$ crystals were also prepared using the above method in CB/DMF (50 °C) and CB/DMSO (40 °C) respectively. More details are provided in Table S1

Table S1. Crystal growth of $MAPbI_3$, $MAPbBr_3$ and $MAPbCl_3$ in different conditions.

	Solvent	**$MAPbX_3$ solution (ml)**	**CB added (ml)**	**Crystal growth temperature (°C)**
$MAPbI_3$	GBL	10	5.5	60
$MAPbBr_3$	DMF	10	1.8	50
$MAPbCl_3$	DMSO	10	7	40

Single-crystal determination

X-ray diffraction data collection for $MAPbI_3$ was performed on a Rigaku Mercury CCD diffractometer with Mo-Kα radiation (λ = 0.71073 Å) at 293(2) K. The data sets were corrected for Lorentz and polarization factors as well as absorption by the multi-scan method [1]. The structure was solved by the direct method and refined by full-matrix least-squares fitting on F^2 by SHELX-97 [2]. All non-hydrogen atoms were refined with anisotropic thermal parameters. The structure contains

substitutional disorder in which C1 and N1 occupy the same position, thus C and N atoms were refined with 'EDAP' and 'EXYZ' constraint instructions. The ratio of C1 and N1 was fixed to 1: 1 to achieve charge balance. All the H atoms in $MAPbI_3$ were assigned to protonated MA molecules on account of charge balance, but they were not refined due to the difficulty in the determination of their precise locations. The structure of compounds was also checked for possible missing symmetry with PLATON.

Other characterizations

Fourier transform infrared (FTIR, Agilent Cary 5000) spectroscopy was conducted with a spectrometer (Thermo Nicolet) with KBr pellets for test the powdered $MAPbI_3$.

X-ray photoelectron spectroscopic (XPS, ESCLAB250) measurements were carried out by using a monochromated Al Kα X-ray source at power of 150 W.

Raman spectra of $MAPbI_3$ single crystal were collected by employing Lab Ram HR Evolution. The system has been calibrated against the 520.5 cm^{-1} line of an internal silicon wafer. The excitation used consists of a diode laser at 532 nm. The spectra have been registered in the 50–500 cm^{-1} range, particularly sensitive the MA cation and Pb–I modes. The laser power intensity with 1% − 5% of 300 W has been kept to avoid any sample degradation effects.

Thermo-gravitometry (TG) and differential scanning calorimetry (DSC) analysis was carried out by using a simultaneous thermal analyzer (STA409C, Netzsch, Germany) to test phase transition and stability of powdered $MAPbI_3$ from room temperature to 150 °C with a step of 5 $°C\ min^{-1}$.

Table S2. Bond lengths [Å] and angles [deg] for Cubic $MAPbI_3$.

Pb(1)-I(2)#1	**3.1361(6)**
Pb(1)-I(2)	3.1361(6)
Pb(1)-I(2)#2	3.1361(6)
Pb(1)-I(2)#3	3.1361(6)
Pb(1)-I(2)#4	3.1361(6)
Pb(1)-I(2)#5	3.1361(6)
I(2)-Pb(1)#6	3.1361(6)
I(2)#1-Pb(1)-I(2)	90.0
I(2)#1-Pb(1)-I(2)#2	90.0
I(2)-Pb(1)-I(2)#2	180.0
I(2)#1-Pb(1)-I(2)#3	90.0
I(2)-Pb(1)-I(2)#3	90.0
I(2)#2-Pb(1)-I(2)#3	90.0
I(2)#1-Pb(1)-I(2)#4	90.0
I(2)-Pb(1)-I(2)#4	90.0
I(2)#2-Pb(1)-I(2)#4	90.0
I(2)#3-Pb(1)-I(2)#4	180.0
I(2)#1-Pb(1)-I(2)#5	180.0
I(2)-Pb(1)-I(2)#5	90.0
I(2)#2-Pb(1)-I(2)#5	90.0
I(2)#3-Pb(1)-I(2)#5	90.0
I(2)#4-Pb(1)-I(2)#5	90.0
Pb(1)#6-I(2)-Pb(1)	180.0

Symmetry transformations used to generate equivalent atoms:

#1 z, x, y #2 x, y-1, z #3 -y, x, z #4 -y+1, x, z #5 z, x, y-1 #6 x, y+1, z

Table S3. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for $MAPbI_3$.

	x	y	z	U(eq)
Pb(1)	0	0	0	26(1)
I(2)	0	5000	0	133(3)
N(1)	5000	5000	5000	190(50)
C(1)	5000	5000	5000	190(50)

U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

Table S4. Anisotropic displacement parameters (A^2 x 10^3) for Cubic $MAPbI_3$.

	U11	U22	U33	U23	U13	U12
Pb(1)	26(1)	26(1)	26(1)	0	0	0
I(2)	189(5)	23(2)	189(5)	0	0	0
N(1)	190(50)	190(50)	190(50)	0	0	0
C(1)	190(50)	190(50)	190(50)	0	0	0

The anisotropic displacement factor exponent takes the form: -2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

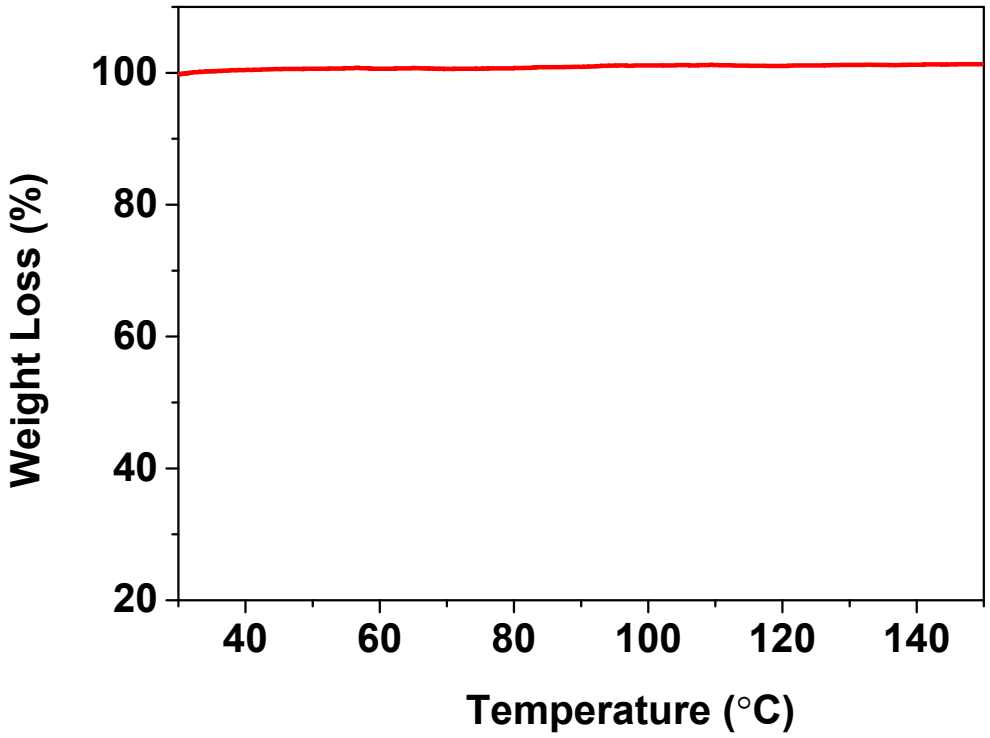

Figure S1. TGA curve of cubic $MAPbI_3$ with temperature range of 30-150 °C.

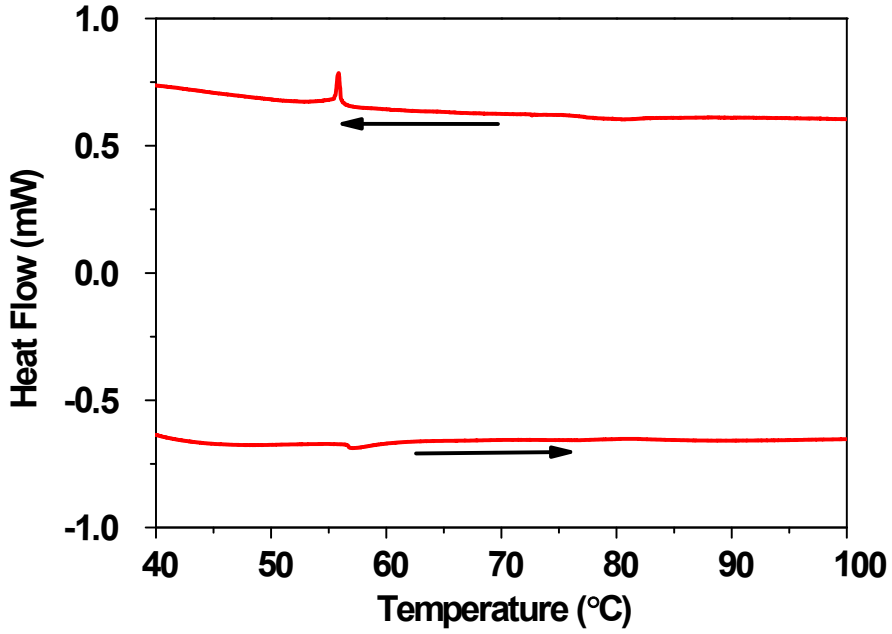

Figure S2. DSC curves of cubic $MAPbI_3$ after stored nearly six months in CB at room temperature.

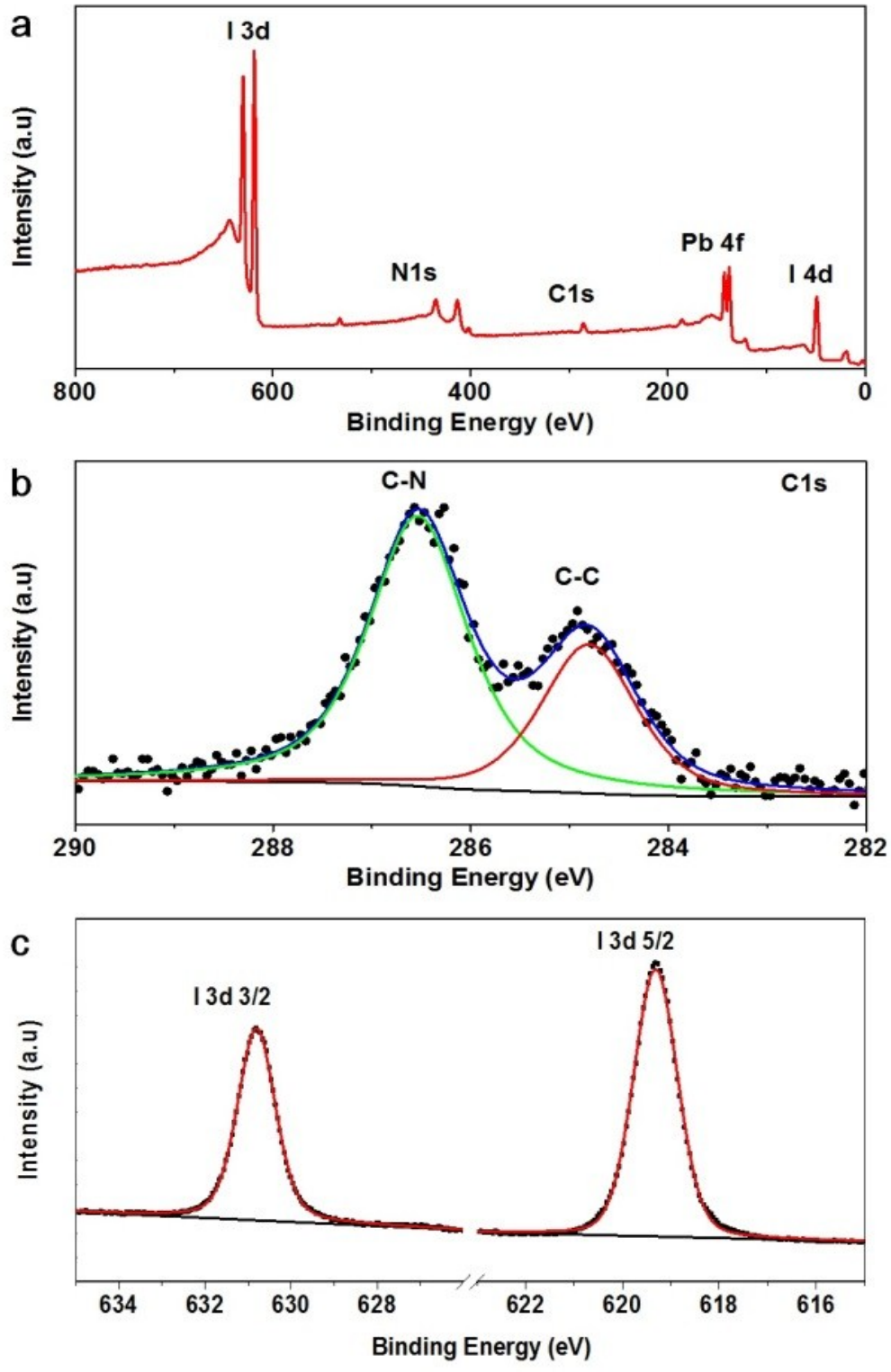

Figure S3. XPS spectra of cubic $CH_3NH_3PbI_3$: a) Full XPS spectrum; b–d) High-resolution core level spectra of C 1s, Pb 4f and I 3d respectively.

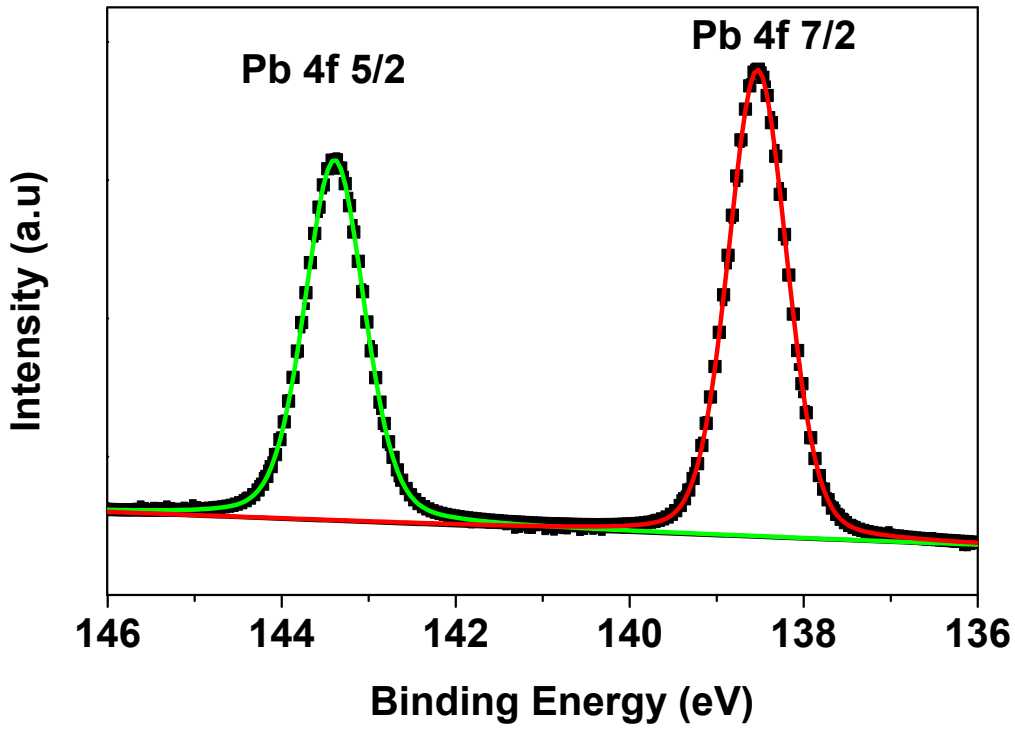

Figure S4. High-resolution core level spectra of Pb 4f.

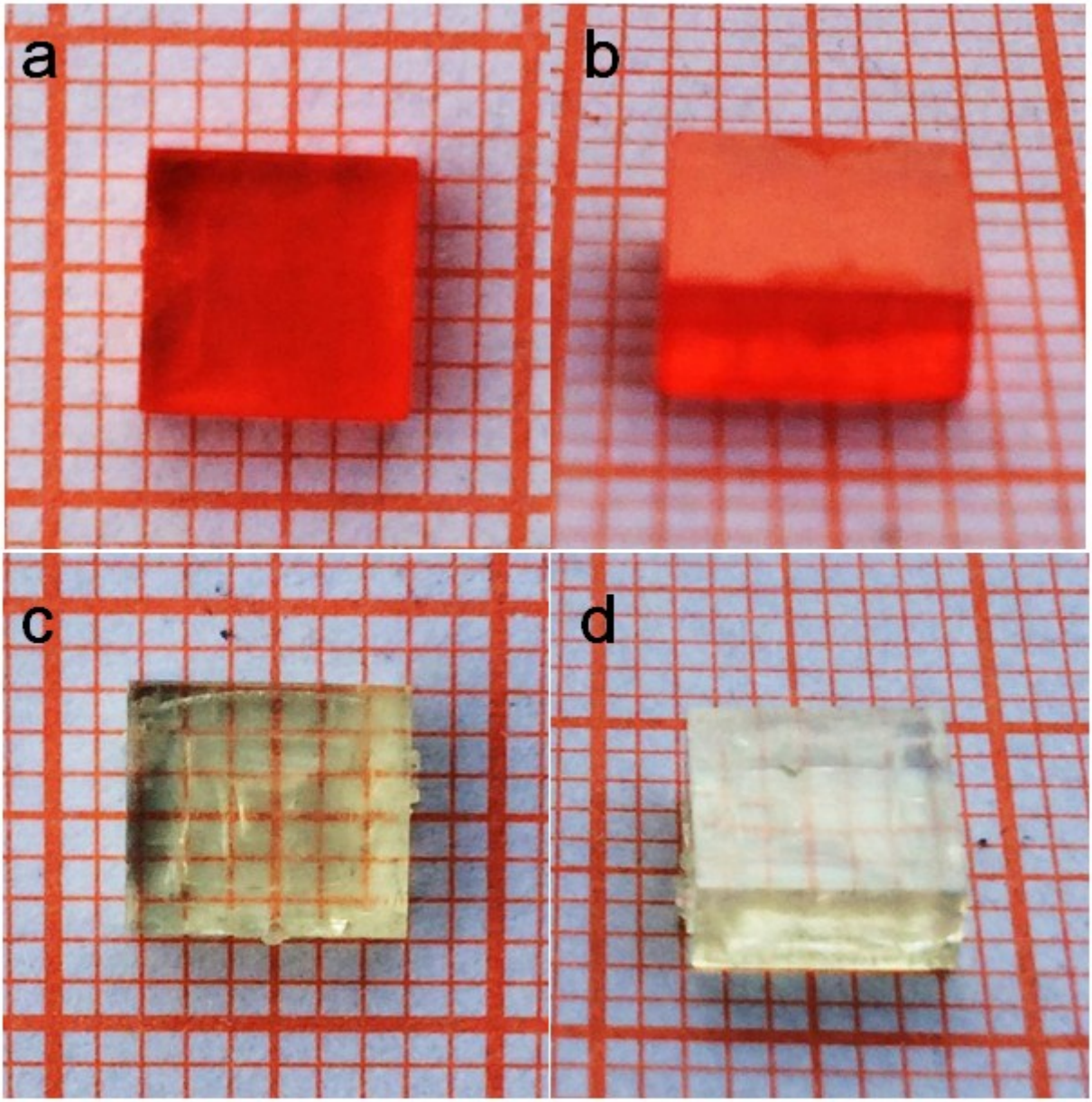

Figure S5. Top-view and side-view pictures of $MAPbX_3$ single crystals: (a-b) $MAPbBr_3$ single crystal (c-d) $MAPbCl_3$ single crystal.

References

1. (a) CrystalClear, Version 1.3.5; Rigaku Corp.: Woodlands, TX, 1999. (b) G. M. Sheldrick, SHELXTL, Crystallographic Software Package, SHELXTL, Version 5.1; Bruker-AXS: Madison, WI, 1998. (c) A. L. Spek, J. Appl. Crystallogr., 36 (2003), p.7.

2. (a) I. D. Brown and D. Altermatt, Acta Crystallogr. B 41(1985), p.244; (b) N. E. Brese and M. O'Keeffe, Acta Crystallogr. B 47(1991), p.192.