

**S1 – Atomic parameters of the ambient pressure La<sub>4</sub>Cu<sub>3</sub>MoO<sub>12</sub> structure**

Atoms	Wyckoff positions	x	y	z	B <sub>iso</sub>	Occupancy
La	2a	0.	0.	0.	0.20(3)	1.
Cu	6h	0.297(3)	0.595(3)	0.25	0.3(2)	1/4
Mo	6h	0.297(3)	0.595(3)	0.25	0.3(2)	1/12
O(1)	6h	0.035(6)	0.069(6)	0.25	1.	1/3
O(2)	4f	1/3	2/3	0.0779(9)	1.	1.

Note: All ambient pressure structure data is based on the best Rietveld refinement with a simple hexagonal unit cell and reflects the average positions of the atoms. The precise structure is unknown.

The thermal factors, B<sub>iso</sub>, were constrained to be equal for the Cu and the Mo atoms and were set equal to 1.0 for the oxygen atoms.

**S2 – Atomic parameters of the high pressure La<sub>4</sub>Cu<sub>3</sub>MoO<sub>12</sub> structure**

Atoms	Wyckoff positions	x	y	z	B <sub>iso</sub>	Occupancy
La(1)	2e	0.215(1)	0.25	0.283(1)	0.5	1.
La(2)	2e	0.205(1)	0.25	0.771(1)	0.5	1.
La(3)	2e	0.750(2)	0.25	0.781(2)	0.5	1.
La(4)	2e	0.741(1)	0.25	0.279(2)	0.5	1.
Cu(1)	2a	0.	0.	0.	0.5	1.
Cu(2)	2c	0.	0.	0.5	0.5	1.
Cu(3)	2b	0.5	0.	0.	0.6	½
Mo(3)	2b	0.5	0.	0.	0.6	½
Cu(4)	2d	0.5	0.	0.5	0.6	½
Mo(4)	2d	0.5	0.	0.5	0.6	½
O(1)	4f	0.000(5)	-0.063(4)	0.261(4)	1.	1.
O(2)	4f	0.285(4)	-0.056(6)	-0.032(6)	1.	1.
O(3)	4f	0.269(4)	0.025(6)	0.564(6)	1.	1.
O(4)	4f	0.411(4)	0.044(5)	0.251(5)	1.	1.
O(5)	2e	-0.008(8)	0.25	0.005(8)	1.	1.
O(6)	2e	0.465(7)	0.25	-0.118(6)	1.	1.
O(7)	2e	0.581(6)	0.25	0.547(7)	1.	1.
O(8)	2e	0.016(7)	0.25	0.460(8)	1.	1.

Note: The thermal factors, B<sub>iso</sub>, were all fixed.

**S3 – Distances (Å) in the ambient pressure  $\text{La}_4\text{Cu}_3\text{MoO}_{12}$  structure**

La-O(1) 2.760(2) x 2

La-O(2) 2.438(3) x 6

In plane distances :

Cu/Mo-O(1) 1.80(2) x 1/3

Cu/Mo-O(1) 2.16(2) x 2/3

Cu/Mo-O(1) 2.18(3) x 2/3

Cu/Mo-O(1) 2.52(3) x 2/3

Cu/Mo-O(1) 2.56(3) x 2/3

Apical distances :

Cu/Mo-O(2) 1.909(9) x 2

**S4 – Distances (Å) and selected angles (°) in the high pressure La<sub>4</sub>Cu<sub>3</sub>MoO<sub>12</sub> structure**

La(1)-O(8)	2.19(6)	x 1	La(2)-O(1)	2.23(4)	x 2
La(1)-O(4)	2.29(4)	x 2	La(2)-O(6)	2.28(6)	x 1
La(1)-O(5)	2.80(7)	x 1	La(2)-O(3)	2.46(5)	x 2
La(1)-O(3)	2.84(5)	x 2	La(2)-O(5)	2.59(7)	x 1
La(1)-O(1)	3.02(4)	x 2	La(2)-O(8)	2.84(6)	x 1
La(1)-O(2)	3.49(5)	x 2	La(2)-O(2)	2.90(5)	x 2
La(3)-O(7)	2.27(5)	x 1	La(4)-O(3)	2.47(4)	x 2
La(3)-O(2)	2.50(5)	x 2	La(4)-O(2)	2.47(5)	x 2
La(3)-O(6)	2.51(6)	x 1	La(4)-O(7)	2.52(5)	x 1
La(3)-O(1)	2.55(4)	x 2	La(4)-O(8)	2.63(6)	x 1
La(3)-O(5)	2.60(7)	x 1	La(4)-O(5)	3.04(7)	x 1
La(3)-O(4)	2.65(4)	x 2	La(4)-O(4)	3.16(3)	x 2
La(3)-O(8)	3.40(6)	x 1	La(4)-O(1)	3.25(4)	x 2
La(3)-O(3)	3.46(5)	x 2			

**In plane distances :**

Cu(1)-O(5)	1.947(3)	x 2
Cu(1)-O(1)	2.11(3)	x 2
Cu(2)-O(1)	1.94(3)	x 2
Cu(2)-O(8)	1.98(1)	x 2
Cu(3)/Mo(3)-O(4)	2.16(4)	x 2
Cu(3)/Mo(3)-O(6)	2.17(2)	x 2
Cu(4)/Mo(4)-O(4)	2.09(4)	x 2
Cu(4)/Mo(4)-O(7)	2.09(2)	x 2

**Apical distances :**

Cu(1)-O(2)	2.41(3)	x 2
Cu(2)-O(3)	2.26(3)	x 2
Cu(3)/Mo(3)-O(2)	1.83(3)	x 2
Cu(4)/Mo(4)-O(3)	1.99(3)	x 2

Cu(1)-O(5)-Cu(1)	175.3(1)
Cu(2)-O(8)-Cu(2)	159.9(5)
Cu(1)-O(1)-Cu(2)	152(1)

average Cu-O-Cu 162(1)

**S5 – Crystallographic data for the ambient and high pressure La<sub>4</sub>Cu<sub>3</sub>MoO<sub>12</sub> structures**

Formula	(AP) La <sub>4</sub> Cu <sub>3</sub> MoO <sub>12</sub>	(HP) La <sub>4</sub> Cu <sub>3</sub> MoO <sub>12</sub>
space group	P6 <sub>3</sub> /mmc	P2 <sub>1</sub> /m
a (Å)	3.95303(5)	8.2354(5)
b (Å)	3.95303(5)	7.7809(4)
c (Å)	10.9997(2)	7.8572(4)
β (°)	-	92.155(2)
V (Å <sup>3</sup> )	148.9	503.1
Z	0.5	2
d <sub>calc</sub> (g.cm <sup>-3</sup> )	5.77	6.83
Radiation	CuKα	CuKα
Monochromator	Graphite	Graphite
2θ range (°), step	3-120	3-120
Software used	Fullprof 3.1 January 96	Fullprof 3.1 January 96
R <sub>p</sub> (%)	6.60	3.83
R <sub>wp</sub>	9.60	5.55
R <sub>exp</sub> (%)	6.94	4.77
Chi <sup>2</sup>	1.91	1.35
R <sub>Bragg</sub> (%)	6.63	8.18
R <sub>f</sub> (%)	5.29	7.31
# reflections	120	1630
# refined parameters	22	47
Profile function and parameters	Pseudo-Voigt p(x) = η*L(x) + (1-η)G(x)	Pseudo-Voigt p(x) = η*L(x) + (1-η)G(x)
η	0.59(1)	0.97(2)
U	0.048(2)	0.19(2)
V	-0.040(2)	-0.11(1)
W	0.0169(6)	0.040(3)
Preferred Orientation Correction	March's function Orientation direction : 1 0 0 G1 = 0.927(3), G2 = 0.	March's function Orientation direction : 1 0 0 G1 = 1.021(3), G2 = 0.
Asymmetry Correction	Berar & Baldinozzi (J.Appl. cryst., 26, 128, (1993) P(1) = 0.208(6) P(2) = 0.055(3) P(3) = 0, P(4) = 0	Berar & Baldinozzi (J.Appl. cryst., 26, 128, (1993) P(1) = 0.158(6) P(2) = 0.019(2) P(3) = 0, P(4) = 0
Background Correction	polynomial function with 6 variables B1 = 134(1), B2 = 43(3) B3 = -23(6), B4 = -106(8) B5 = 132(12), B6 = -41(4)	polynomial function with 6 variables B1 = 313.9(8), B2 = 86(2) B3 = -21(5), B4 = -126(4) B5 = 132(8), B6 = -37(3)