Detailed results of the electron diffraction on the two phases in the quenched sample and the third phase in the slow-cooled sample

Three different phases were identified using electron diffraction: two in the quenched sample (phase 1 and phase 2) and one in the slow-cooled sample (phase 3). The supercells and symmetries of all three were investigated with LATED and CBED.

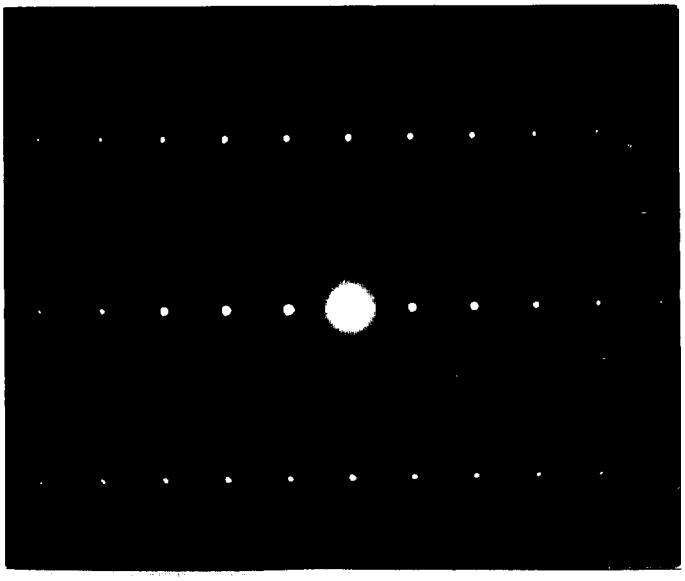
Page S4 shows a set of LATED patterns obtained from 1 in the quenched sample by tilting around the 000ℓ row. The reconstructed reciprocal plane has hexagonal symmetry and the deduced extinction of the hh-2hℓ reflections is $\ell = 2n + 1$. Based on this information, five space groups are possible: P31c (C^4_{3v}), P-31c (D^2_{3d}), P6_3mc (C^4_{6v}), P-62c (D^4_{3h}) and P6_3/mmc (D^4_{6h}). The first four are non-centrosymmetric and the last one is centrosymmetric. The CBED patterns taken along [11-20] reveal the black bands, or G-M lines in the 000ℓ discs for odd ℓ (page S5). This confirms the presence of a screw axis in the *c* direction. P31c, P-31c, and P-62c do not contain a screw axis so this leaves P6_3mc and P6_3/mmc. The obvious difference between these two choices is a second mirror plane perpendicular to the *c* axis. CBED along [11-20] clearly shows both mirror planes, so the correct space group is P6_3/mmc. The measured parameters of the hexagonal lattice are approximately $a = 4$ and $c = 11$ Å.

Page S6 shows a set of LATED diffraction patterns of 2 which is also in the quenched sample. These patterns were also taken around the 00ℓ row for equivalent zone axes to the previous set (page S4). Extra reflections appear along the [100] and [110] directions in addition to the diffusion lines. These satellite reflections indicate the presence of an alternate symmetry because they are not consistent with hexagonal symmetry. The limitation for h0ℓ reflections is $h + \ell = 2n + 1$ (page S6 figure (c)), and the reconstructed reciprocal lattice is orthorhombic. There are only two space groups that fit the observed extinction reflections; one is centrosymmetric Pmnm (D^{13}_{2h}) and the other is non-centrosymmetric Pmn2_1 (C^7_{2v}). Two mirror planes perpendicular to the *b* axis, which can be seen in

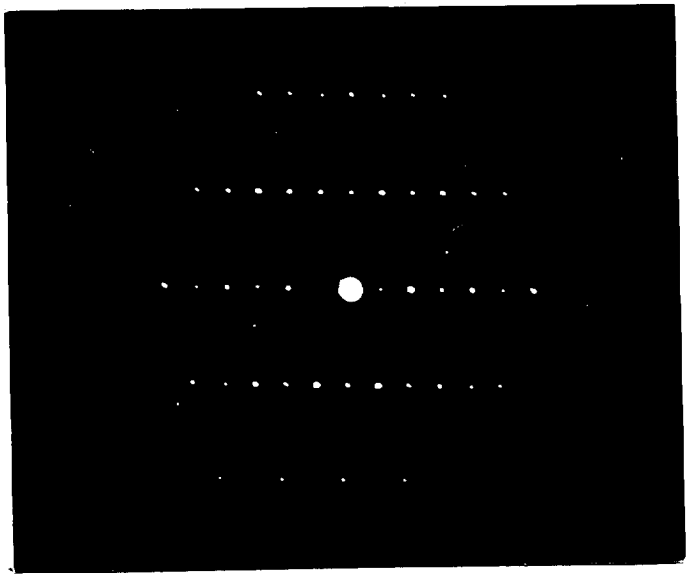
the CBED pattern along the [010] direction, indicates that Pmnm is the correct space group (page S7). Note that Pmnm is a subgroup of Cmcm, which in turn is a sub group of $P6_3/mmc$. The measured lattice parameters are $a_o = a_h = 4$ Å, and $b_o = \sqrt{3}a_h = 6.9$ Å, and $c_o = c_h = 11$ Å. The subscripts *h* and *o* designate the hexagonal and orthorhombic cells, respectively.

The orthorhombic phase is closely related to the hexagonal phase, and the diffuse lines pictured on page S6 suggest that even the orthorhombic phase is only partially ordered. We now examine 3 which is the only phase found in the slow-cooled sample. It should exhibit optimal cation ordering. Page S8 shows the LATED diffraction patterns with the incident beam parallel to the same zone axes as those on page S4 and S6. The notable feature of this set of patterns is the presence of discrete reflections at the same positions as the diffuse lines of page S6. This confirms additional order in the cation lattice. Both the real and the reciprocal space lattices are orthorhombic with the *b* and *c* axes the same length as before, however, the *a* axis is doubled. The $\ell = 2n + 1$ reflection extinction rule was found along the 00l row, and therefore the possible space groups are $P222_1$ and $P112_1/m$. As before, these two groups can be distinguished by the presence of a mirror plane perpendicular to the screw axis, and again the CBED pattern taken along the [010] direction shows the mirror plane perpendicular to the *c* axis indicating that the space group is indeed $P112_1/m$ (page S9). Measured lattice parameters for this monoclinic ordered phase are: $a_m = 2a_h = 8$ Å, $b_m = \sqrt{3}a_h = 6.9$ Å, $c_m = c_h = 11$ Å, and $\gamma = 90°$, where the subscript *m* designates the monoclinic cell. It is important to remember that while the unit cell for this phase is orthorhombic, the symmetry is monoclinic after the doubling of the *a*-axis.

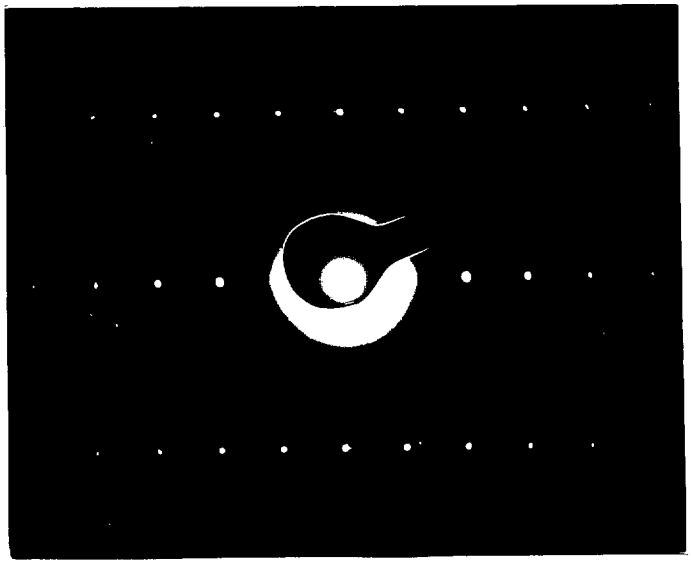
ED of the quenched sample tilted around the 00ℓ row which evidences the formation of phase 1



a) LATED pattern along [10-10] zone axis

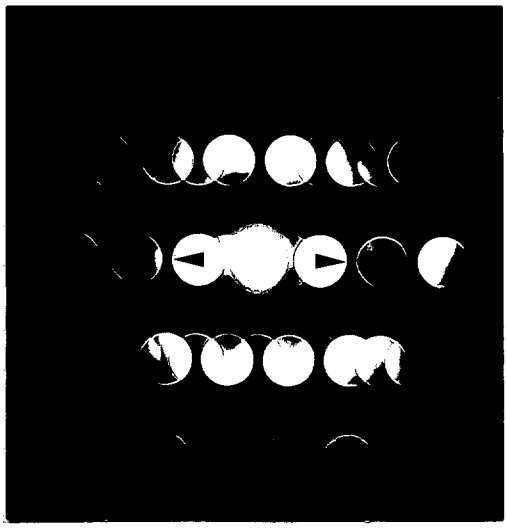


b) LATED pattern along [11-20] zone axis

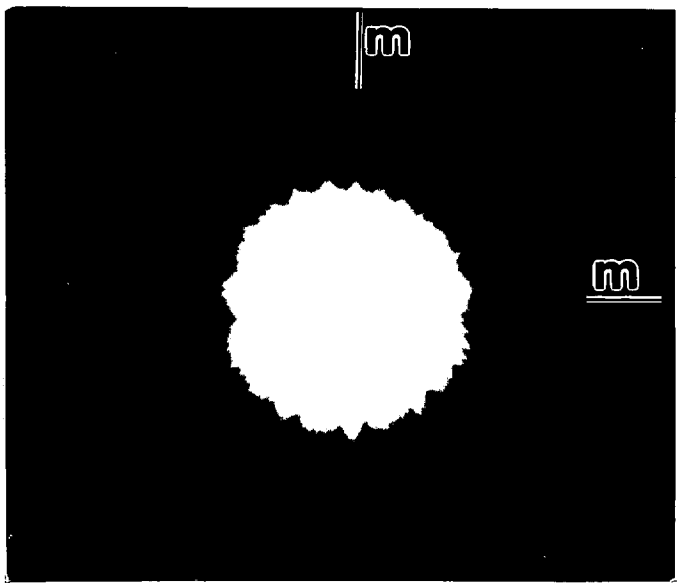


c) LATED pattern along [01-10] zone axis

CBED images along [11-20] zone axis for phase 1

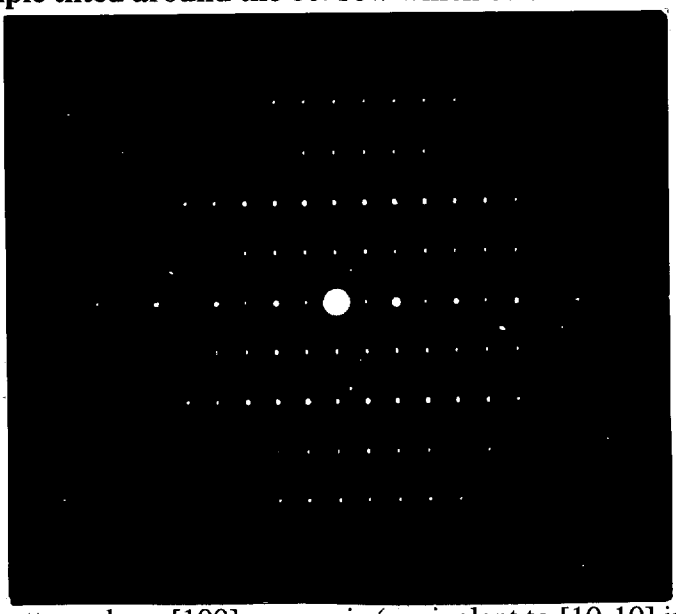


a) G-M lines (marked by arrows) in the 000ℓ discs for odd ℓ indicative of the screw axis in the *c* direction.

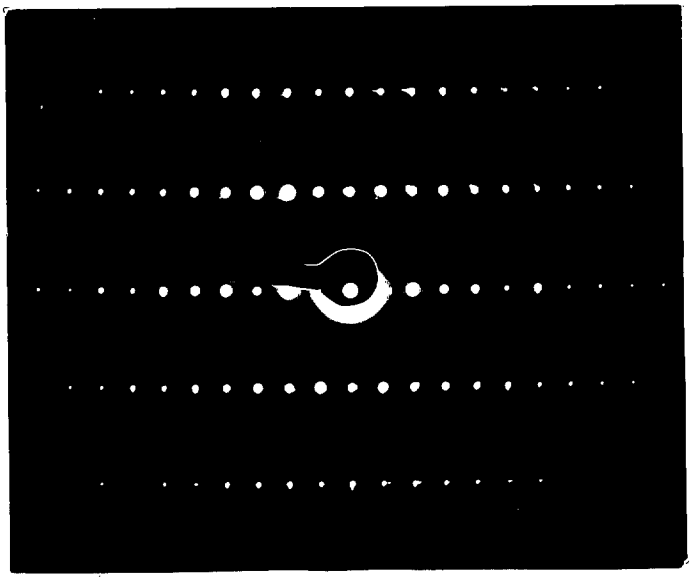


b) Two mirror planes perpendicular to the *c*-axis

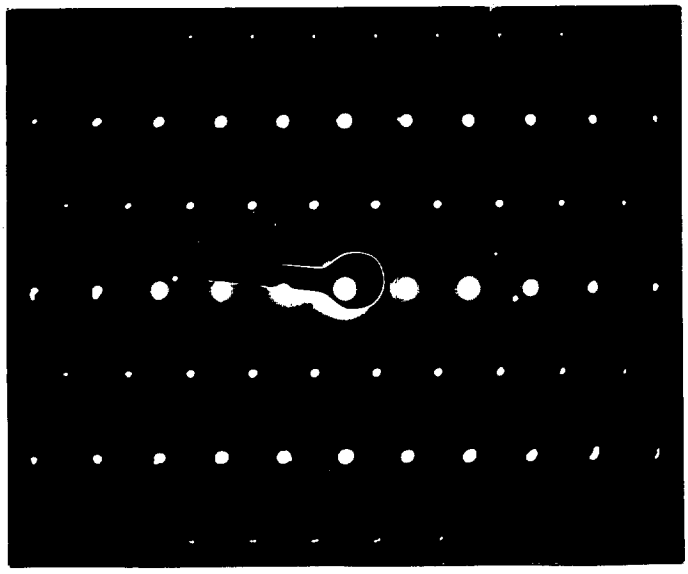
ED of the quenched sample tilted around the 00ℓ row which evidences the formation of phase 2



a) LATED pattern along [100] zone axis (equivalent to [10-10] in hexagonal indices)

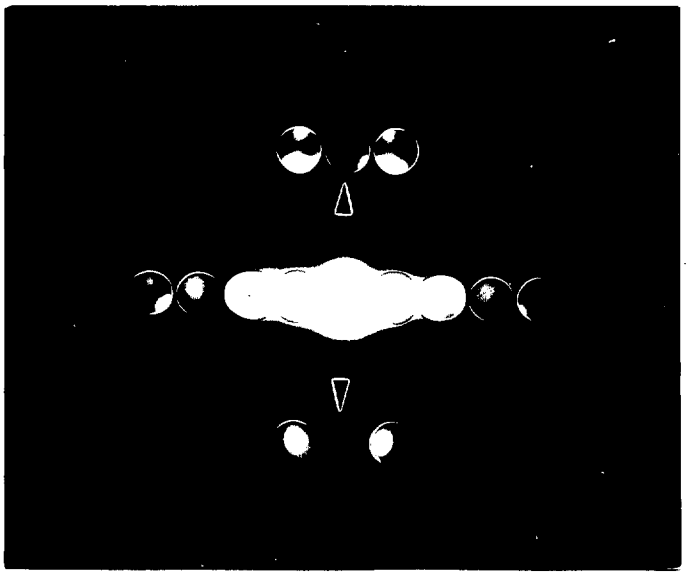


b) LATED pattern along [110] zone axis (equivalent to [11-20] in hexagonal indices)

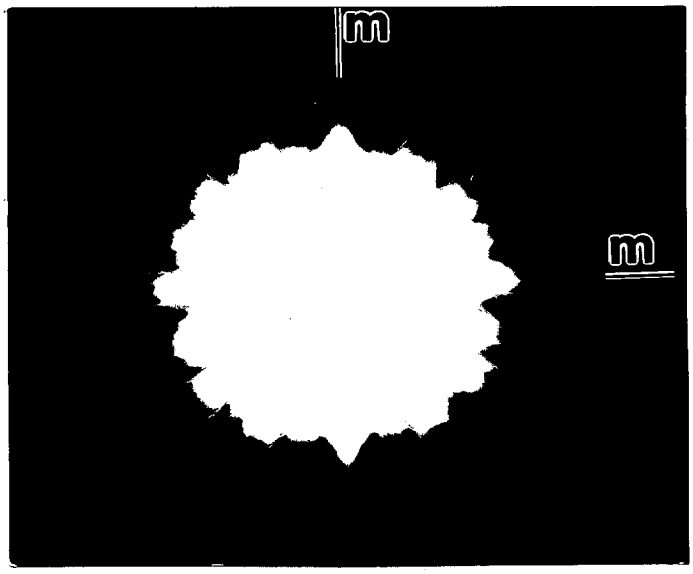


c) LATED pattern along [010] zone axis (equivalent to [1-210] in hexagonal indices)

CBED images for phase 2

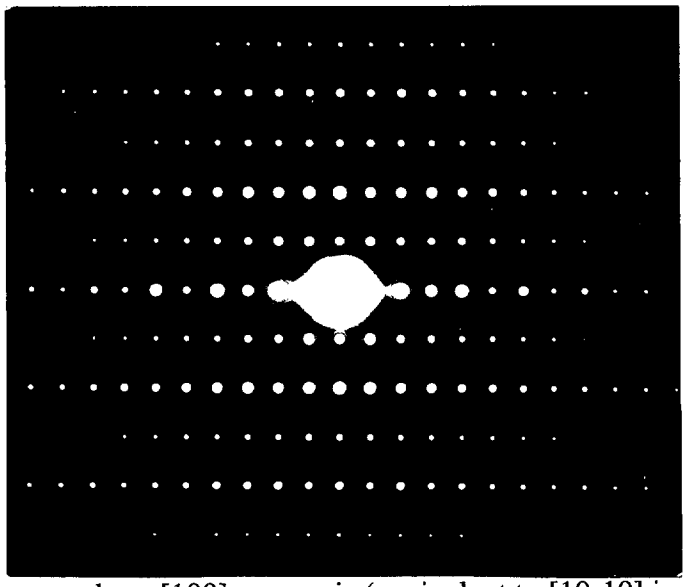


a) G-M lines along [201] (marked by arrows) in the h0ℓ discs for odd h+ℓ indicative of the (a+c)/2 glide operation.

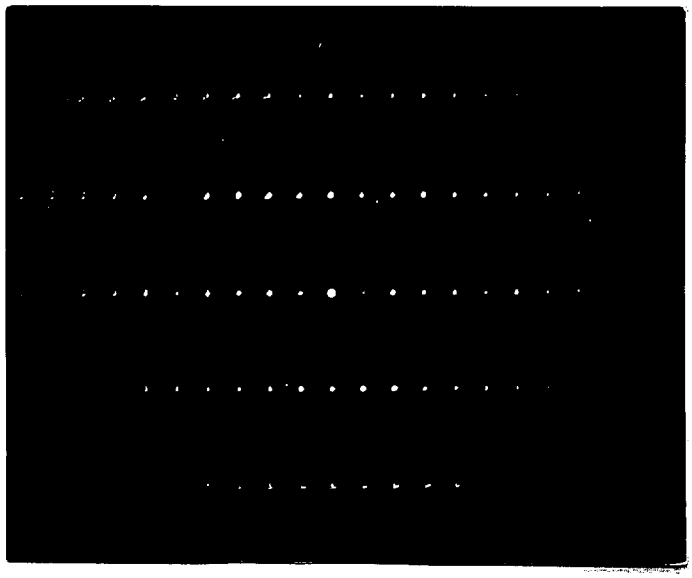


b) CBED image along [010] showing two mirror planes perpendicular to the *b*-axis.

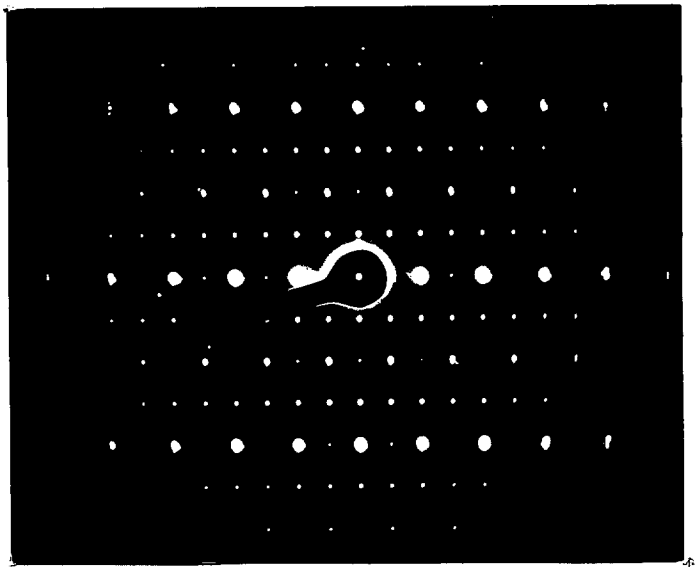
ED of the slow cooled sample tilted around the 00ℓ row which evidences the formation of phase 3



a) LATED pattern along [100] zone axis (equivalent to [10-10] in hexagonal indices)

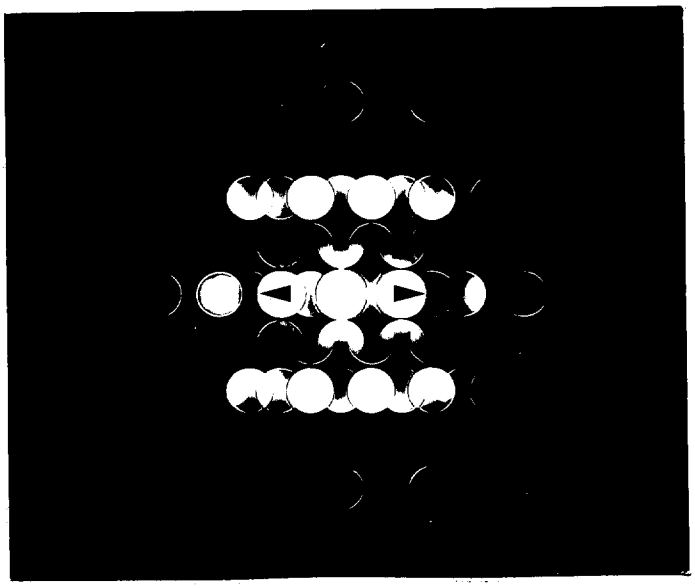


b) LATED pattern along [210] zone axis (equivalent to [11-20] in hexagonal indices)

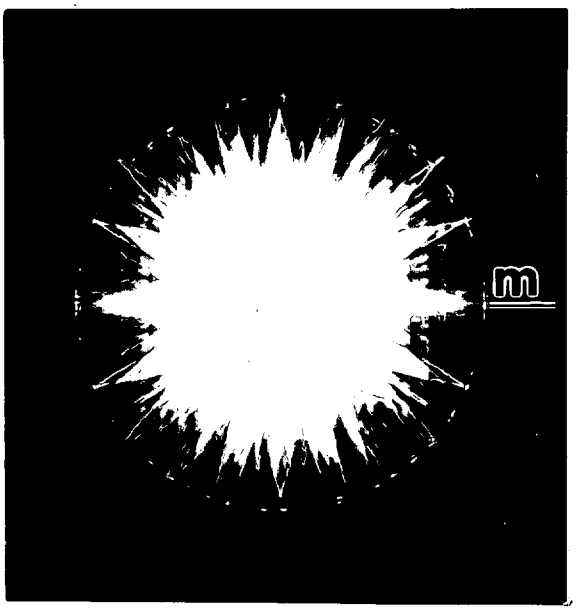


c) LATED pattern along [010] zone axis (equivalent to [1-210] in hexagonal indices)

CBED images along [010] zone axis for phase 3



a) G-M lines (marked by arrows) in the 00ℓ discs for odd ℓ indicative of the screw axis in the *c* direction.



b) The mirror plane perpendicular to the *c*-axis.

Crystallographic data for $La_4Cu_3MoO_{12}$ based on Rietveld refinement of neutron data in $P6_3/mmc$

Atom	Site	*x*	*y*	*z*	Ui/Ueq*100	Occ.
La	2a	0	0	0	0.67(3)	1
(Cu/Mo)	6h	0.2941(4)	0.5882(7)	¼	0.49(6)	$^1/_3$
O1	4f	$^1/_3$	$^2/_3$	0.0836(1)	0.60(3)	1
O2	6h	0.0540(6)	0.1080(2)	¼	2.50	$^1/_3$

$P6_3/mmc$; a = 3.9559(2) Å, c = 11.0120(4) Å; χ^2 = 2.58; R_{F2} = 11.6%.

Crystallographic data for $La_4Cu_3MoO_{12}$ based on Rietveld refinement of neutron data in Pmnm

Atom	Site	*x*	*y*	*z*	Ui/Ue*100	Occ
La *La*	4f	¼ *¼*	0.2435(4) *¼*	-0.0031(3) *0*	0.52(3)	1
(Cu1Mo1) (Cu1/Mo1)' *(Cu/Mo)*	2b	¾ *¾*	0.396(2) 0.463(2) *0.41666*	¼ *¼*	0.2(1) 0.2(1)	½ ½
(Cu2/Mo2) *(Cu/Mo)*	4e	0.200(2) *¼*	0.8835(8) *0.91666*	¼ *¼*	0.4(1)	½
O1 *O1*	4f	¾ *¾*	0.4166(9) *0.41666*	0.0822(3) *0.0836(1)*	0.58(7)	1
O2 *O1*	4f	¼ *¾*	0.9179(9) *0.91666*	0.0854(3) *0.0836(1)*	0.74(7)	1
O3 O3' *O2*	2b	¾ *¾*	0.763(3) 0.694(2) *¾*	¼ *¼*	1.1(2) 1.1(2)	½ ½
O4 *O2*	4e	0.152(2) *¼*	0.298(1) *¼*	¼ *¼*	0.8(2)	½

Pmnm; a = 3.9563(2) Å, b = 6.8505(3) Å, c = 11.0112(2) Å; χ^2 = 1.94; R_{F^2} = 7.3%.

The atomic labels used in the hexagonal model (S10) and ideal hexagonal coordinates are written in italics.

Atomic parameters of the ambient pressure $La_4Cu_3MoO_{12}$ structure

based on the Rietveld refinement of neutron data in $P112_1/m$

Space group $P112_1/m$

$a = 7.9126(4)$ Å
$b = 6.85034(33)$ Å
$c = 11.01145(13)$ Å
$\alpha = 90°$
$\beta = 90°$
$\gamma = 90.027(6)°$
Cell volume = 596.86(4) Å^3

Atomic Positions

Name	Type	X	Y	Z	Ui/Ue*100	SiteSym	Mult
La1	La	0.1227(12)	0.2465(7)	-0.0025(5)	0.41(11)	1	4
La2	La	0.6265(13)	0.2422(7)	0.0019(6)	0.62(11)	1	4
Mo1	Mo	0.3785(29)	0.4223(20)	0.250000	0.30(13)	M(010)	2
Cu1	Cu	0.8782(22)	0.4623(13)	0.250000	0.65(20)	M(010)	2
Cu2	Cu	0.0893(18)	0.8926(16)	0.250000	0.73(25)	M(010)	2
Cu2'	Cu	0.6465(18)	0.8816(15)	0.250000	0.95(26)	M(010)	2
O1	O	0.3787(28)	0.4177(29)	0.0789(8)	0.63(16)	1	4
O1'	O	0.8763(28)	0.4173(31)	0.0835(8)	0.75(17)	1	4
O2	O	0.1295(21)	0.9196(29)	0.0888(15)	0.63(28)	1	4
O2'	O	0.6291(20)	0.9159(27)	0.0837(15)	0.34(24)	1	4
O3	O	0.3932(18)	0.6891(20)	0.250000	1.91(36)	M(010)	2
O3'	O	0.8843(19)	0.7435(23)	0.250000	0.96(17)	M(010)	2
O4	O	0.1765(15)	0.2888(23)	0.250000	0.79(35)	M(010)	2
O4'	O	0.5755(17)	0.2882(22)	0.250000	1.20(34)	M(010)	2

Selected bond lengths for the ambient pressure $La_4Cu_3MoO_{12}$ structure based on the Rietveld refinement of neutron data in $P112_1/m$

Bond	Distance (Å)	Bond	Distance (Å)
La1-O1	2.495(23)	Mo1-O3	1.837(22)
La1-O1'	2.462(21)	Mo1-O4	1.828(25)
La1-O1'	2.476(20)	Mo1-O4'	1.808(24)
La1-O2	2.457(21)	Cu1-O1'	1.864(10)
La1-O2	2.466(21)	Cu1-O1'	1.864(10)
La1-O2'	2.438(18)	Cu1-O3'	1.934(21)
La1-O3'	2.727(5)	Cu1-O4	2.656(24)
La1-O4	2.828(6)	Cu1-O4'	2.668(21)
La2-O1	2.456(21)	Cu2-O2	1.820(17)
La2-O1	2.500(20)	Cu2-O2	1.820(17)
La2-O1'	2.473(25)	Cu2-O3'	1.906(22)
La2-O2	2.447(17)	Cu2-O3	2.780(21)
La2-O2'	2.423(18)	Cu2-O4	2.807(18)
La2-O2'	2.473(20)	Cu2'-O2'	1.840(16)
La2-O3	2.818(7)	Cu2'-O2'	1.840(16)
La2-O4'	2.780(7)	Cu2'-O3	2.387(18)
Mo1-O1	1.879(8)	Cu2'-O3'	2.113(20)
Mo1-O1	1.879(8)	Cu2'-O4'	2.847(18)

Selected bond angles for the ambient pressure $La_4Cu_3MoO_{12}$ structure based on the Rietveld refinement of neutron data in $P112_1/m$

Bond	Angle-degrees
O1-Mo1-O1	177.9(15)
O1-Mo1-O3	91.0(8)
O1-Mo1-O4	89.5(10)
O1-Mo1-O4'	89.5(9)
O1-Mo1-O3	91.0(8)
O1-Mo1-O4	89.5(10)
O1-Mo1-O4'	89.5(9)
O3-Mo1-O4	124.0(14)
O3-Mo1-O4'	116.0(12)
O4-Mo1-O4'	119.9(10)
O1'-Cu1-O1'	160.6(14)
O1'-Cu1-O4'	99.7(13)
O1'-Cu1-O4'	99.7(13)
O2-Cu2-O3	158.0(4)
O2-Cu2-O4	101.0(13)
O3-Cu2-O4	101.0(13)
O2'-Cu2'-O3	163.0(4)
O2'-Cu2'-O4'	97.4(11)
O3-Cu2'-O4'	97.4(11)

Refinement parameters for the ambient pressure $La_4Cu_3MoO_{12}$ structure based on the Rietveld refinement of neutron data in $P6_3/mmc$, Pmnm, and $P112_1/m$

Formula	$La_4Cu_3MoO_{12}$	$La_4Cu_3MoO_{12}$	$La_4Cu_3MoO_{12}$
space group	$P6_3/mmc$	Pmnm	$P112_1/m$
a (Å)	3.9559(2)	3.9563(2)	7.9125(4)
b (Å)	3.9559(2)	6.8505(3)	6.8503(4)
c (Å)	11.0120(4)	11.0112(2)	11.0113(2)
β (°)	-	-	90.027(7)
V (Å^3)	149.24(4)	298.43(4)	596.84(5)
Z	0.5	1	2
d_{calc} (g.cm^{-3})	5.75	5.75	5.75
Radiation	Neutron TOF		
d range (Å)	0.5-4.0		
Software	GSAS		
R_p (%) R_{wp} (%) χ^2 R_f [2](%)	2.58 11.6	1.94 7.3	4.8 7.6 1.5 5.4
reflections			5300
parameters			69
Profile function	Exponential pseudo-Voigt convolution (Von Dreele 1990) (3rd TOF profile function in GSAS)		
Background Correction	Power series: $Q^{2n}/n!$		