

# Supporting Information – In situ synchrotron powder diffraction study of Cd intercalation into Chevrel phases: crystal structure and kinetic effect

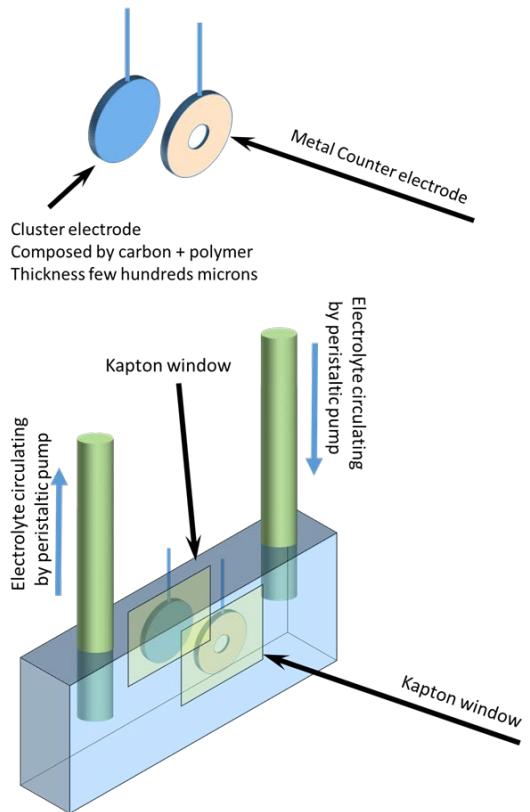
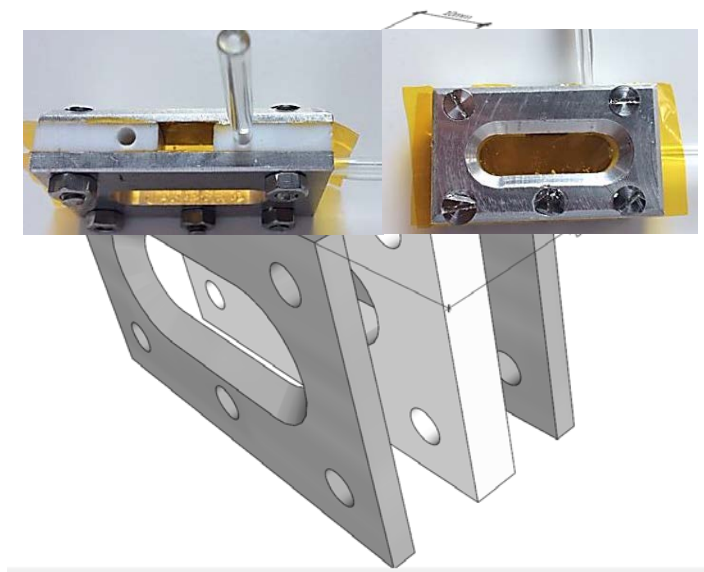
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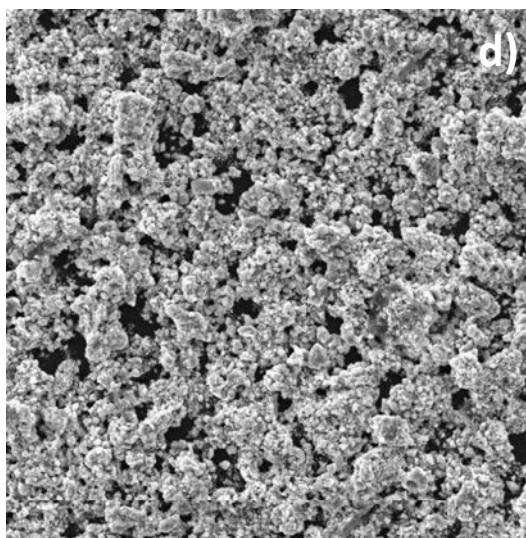
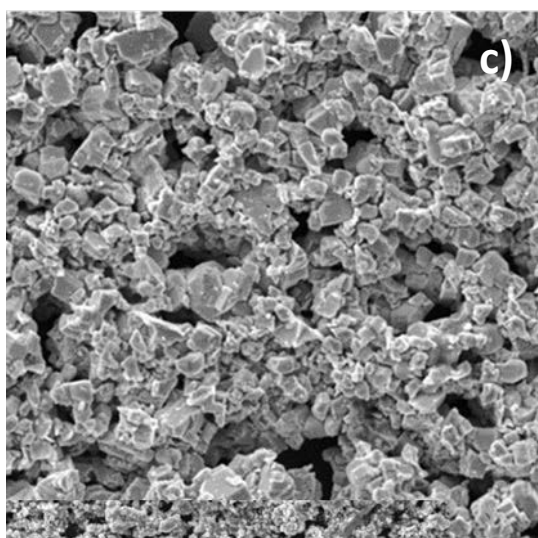
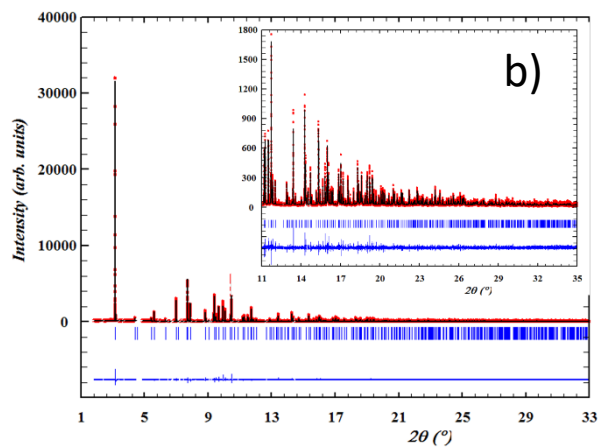
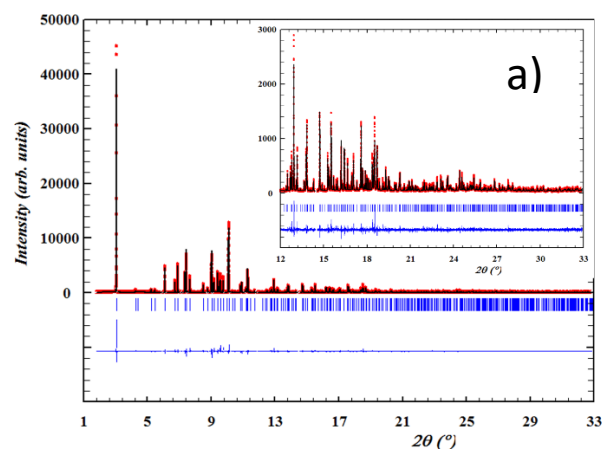
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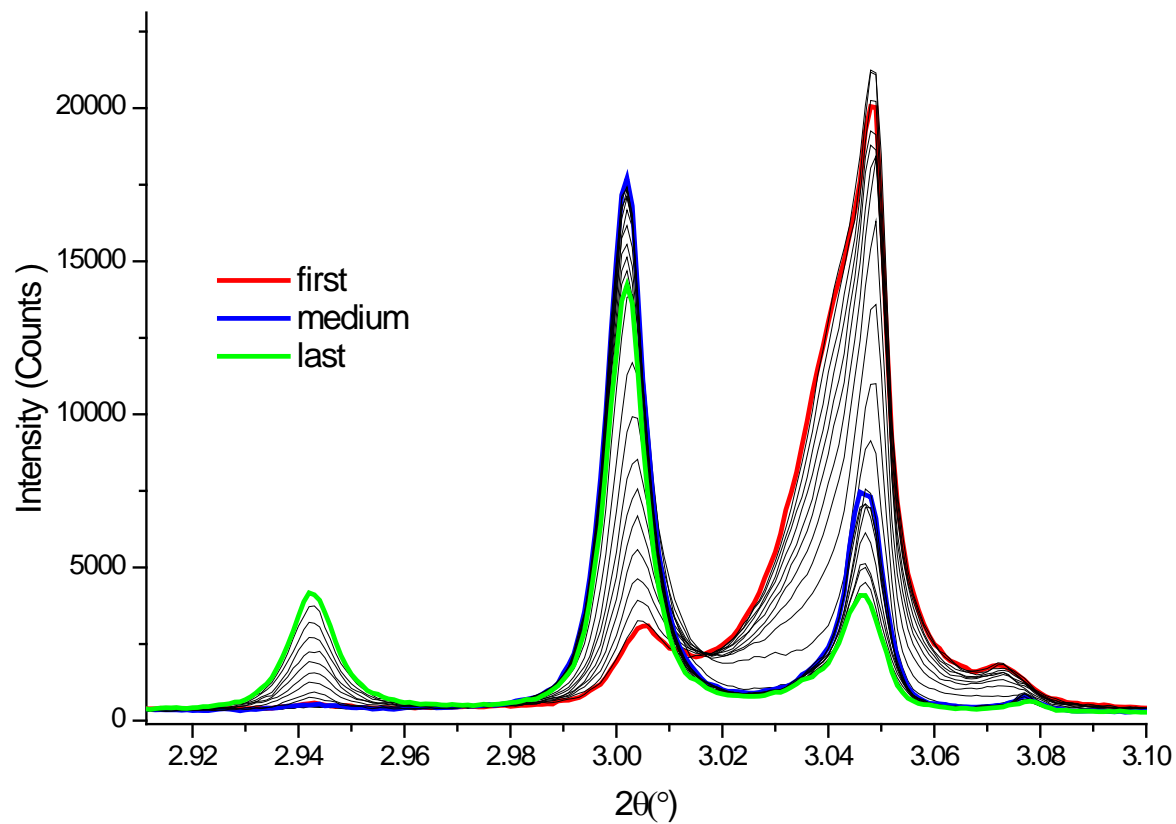
\* [carmelo.prestipino@univ-rennes1.fr](mailto:carmelo.prestipino@univ-rennes1.fr), [olivier.hernandez@univ-rennes1.fr](mailto:olivier.hernandez@univ-rennes1.fr)



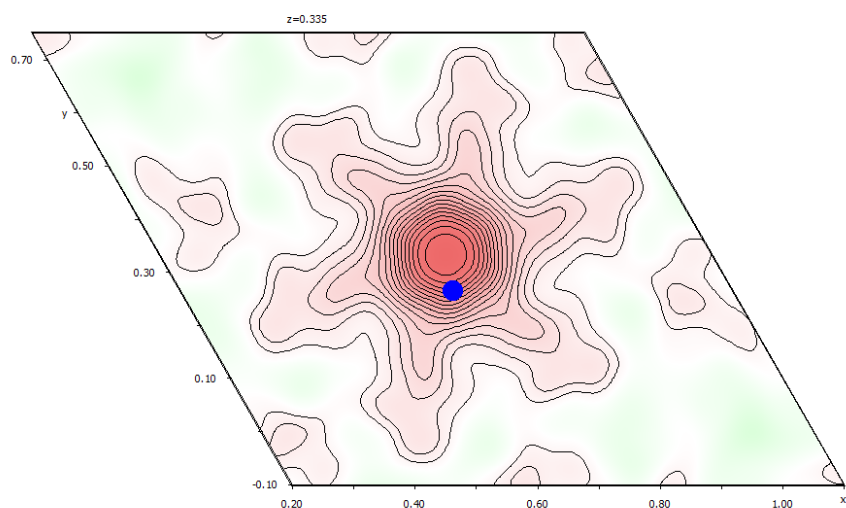
**Figure S1.** Scheme of the electrochemical cell and picture.



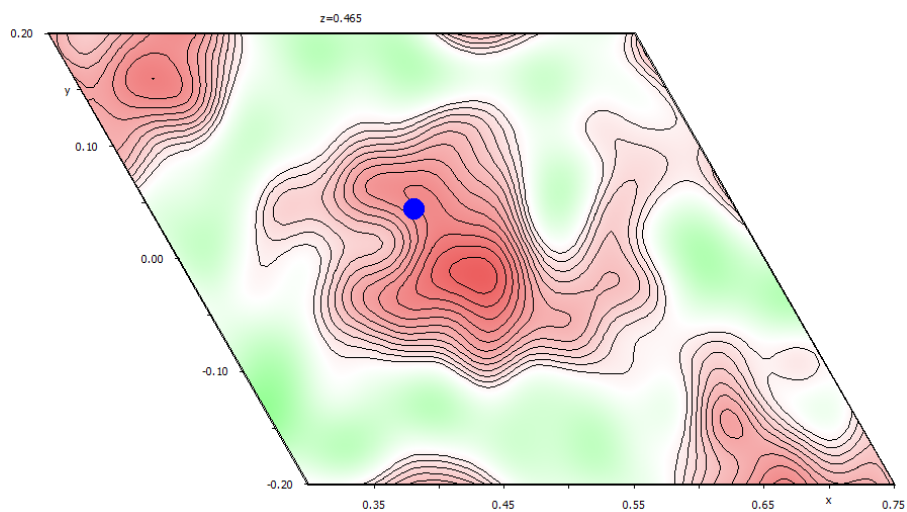
**Figure S2.** Synchrotron Rietveld refinement of  $\text{Mo}_6\text{Se}_8$  and  $\text{Mo}_6\text{S}_8$ , part a) and b), respectively; secondary electron SEM image of c)  $\text{Mo}_6\text{Se}_8$  and d)  $\text{Mo}_6\text{S}_8$ .



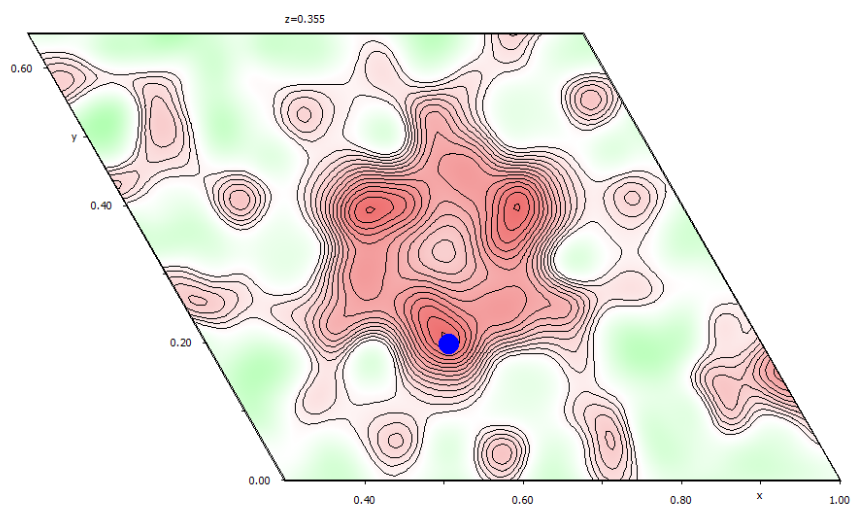
**Figure S3.** Second intercalation at -0.075 mA for  $\text{Mo}_6\text{Se}_8$ . Strong asymmetry on the left of the peak (101) for the binary phase  $\text{Mo}_6\text{Se}_8$  at  $3.05^\circ 2\theta$ .



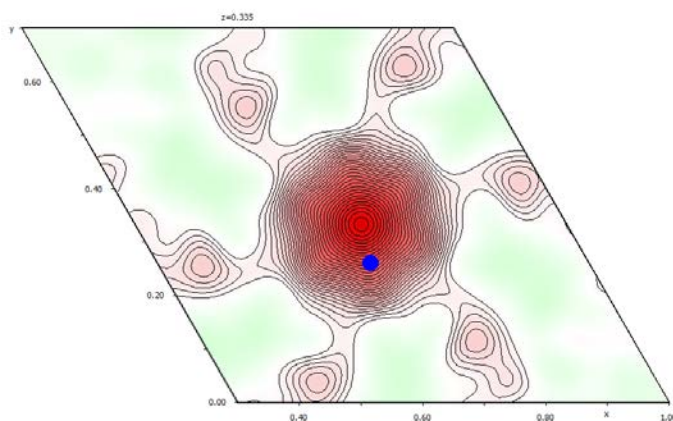
**Figure S4:**  $\text{Cd}_1\text{Mo}_6\text{S}_8$ . Fourier difference map focused on cavity 1,  $x,y$  plane,  $z=0.335$  in the hexagonal cell, Cd refined position marked with the blue circle, positive cutoff  $14.2 \text{ e}^-/\text{\AA}^3$ , positive contour  $0.5 \text{ e}^-/\text{\AA}^3$ .



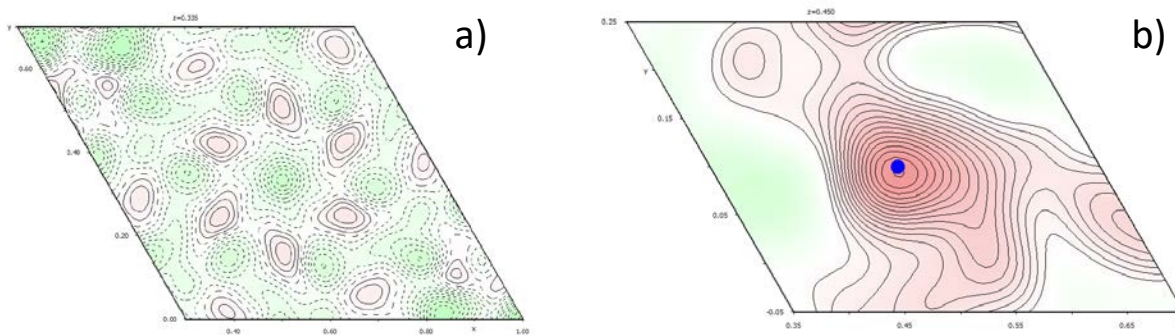
**Figure S5:**  $\text{Cd}_2\text{Mo}_6\text{S}_8$ . Fourier difference map focused on cavity 2,  $x,y$  plane,  $z=0.465$  in the hexagonal cell, Cd refined position marked with the blue circle, positive cutoff  $2.0 \text{ e}^-/\text{\AA}^3$ , positive contour  $0.1 \text{ e}^-/\text{\AA}^3$ .



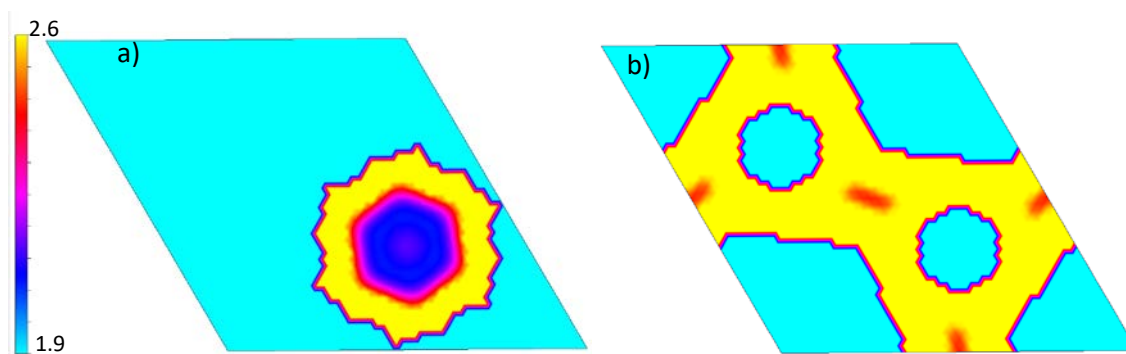
**Figure S6.** Fourier difference map for  $\text{Cd}_2\text{Mo}_6\text{S}_8$  focused on cavity 1,  $x,y$  plane,  $z= 0.355$ , positive cutoff:  $5.0 \text{ e}^-/\text{\AA}^3$ ; contour  $0.2 \text{ e}^-/\text{\AA}^3$ . Cd refined position marked with the blue circle.



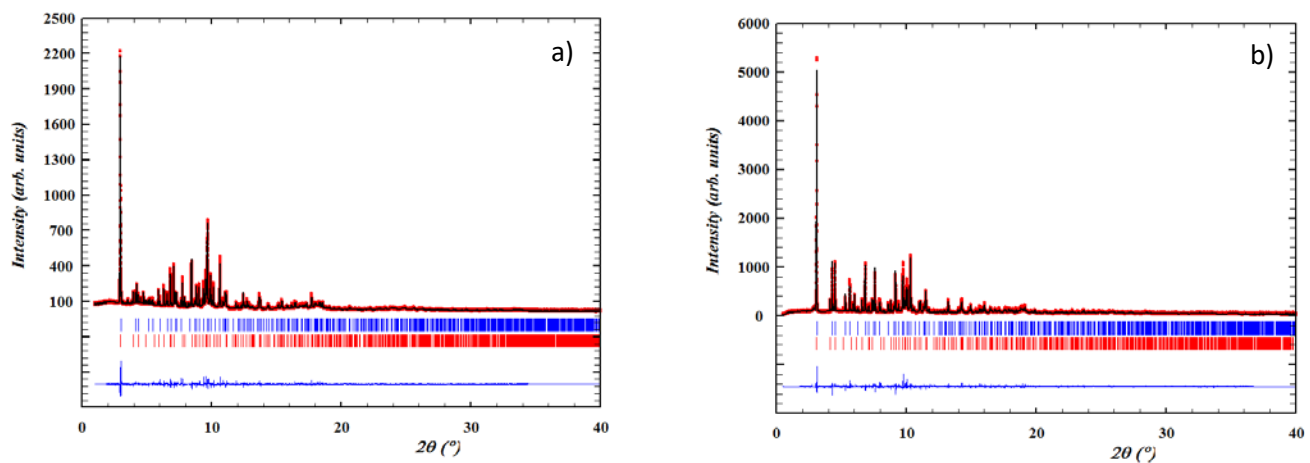
**Figure s7:**  $\text{Cd}_1\text{Mo}_6\text{Se}_8$ . Part a) Fourier difference map focused on cavity 1,  $x,y$  plane,  $z= 0.335$  in the hexagonal cell, Cd refined position marked with the blue circle, positive cutoff  $6.3 \text{ e}^-/\text{\AA}^3$ , positive contour  $0.2 \text{ e}^-/\text{\AA}^3$



**Figure S8:**  $\text{Cd}_2\text{Mo}_6\text{Se}_8$ . Part a) Fourier difference map focused on cavity 1,  $x,y$  plane,  $z=0.335$  (positive/negative cutoff:  $8.4/-2.8 \text{ e}^-/\text{\AA}^3$ ; contour  $0.2 \text{ e}^-/\text{\AA}^3$ ). Part b) Fourier difference map focused on cavity 2,  $x,y$  plane,  $z=0.45$ , positive cutoff:  $8.4 \text{ e}^-/\text{\AA}^3$ ; contour  $0.2 \text{ e}^-/\text{\AA}^3$ . Cd position marked with the blue circle.



**Figure S9.** Valence estimation map in  $\text{Cd}_2\text{Mo}_6\text{Se}_8$  for  $\text{Cd}^{2+}$  obtained by BVS, cavity 1 ( $z=0.333$ ) and cavity 2 ( $z=0.5$ ), part a) and b), respectively. Cyan regions correspond to position not available for  $\text{Cd}^{2+}$  ion or valence higher than 4.



**Figure S10.** Synchrotron Rietveld refinement of  $\text{Cd}_x\text{Mo}_6\text{Se}_8$  and  $\text{Cd}_x\text{Mo}_6\text{S}_8$ , part a) ( $\text{Cd}_1\text{Mo}_6\text{Se}_8$ : 40(1),  $\text{Cd}_2\text{Mo}_6\text{Se}_8$ : 60(1) wgt. %) and b) ( $\text{Cd}_1\text{Mo}_6\text{S}_8$ : 75.0(7),  $\text{Cd}_2\text{Mo}_6\text{S}_8$ : 25.0(15) wgt. %), respectively.



**Table S1.** Interatomic distances in the Mo<sub>6</sub>Se<sub>8</sub> structure.

<b><math>a = 9.56524(4) \text{ \AA}</math></b>	<b><math>c = 11.17121(6) \text{ \AA}</math></b>	<b><math>V = 885.163 \text{ \AA}^3</math></b>		
<b>d (Mo-Mo) (Å)</b>	2.6950(10)	2.8311(10)	3.2686(11)	
<b>d (Mo-Se1) (Å)</b>	2.5722(15)	2.5866(15)	2.5307(11)	2.6004(10)
<b>d (Mo-Se2) (Å)</b>	2.5387(13)			
<b>d (Se1-Se1) (Å)</b>	3.4886(15)			
<b>d (Se1-Se2) (Å)</b>	3.3908(10)			

**Table S2.** Interatomic distances in the Mo<sub>6</sub>S<sub>8</sub> structure.

<b><math>a = 9.19364(2) \text{ \AA}</math></b>	<b><math>c = 10.89026(4) \text{ \AA}</math></b>	<b><math>V = 797.158 \text{ \AA}^3</math></b>		
<b>d (Mo-Mo) (Å)</b>	2.6990(8)	2.8630(9)	3.0837(10)	
<b>d (Mo-S1) (Å)</b>	2.431(2)	2.458(2)	2.4232(18)	2.4240(16)
<b>d (Mo-S2) (Å)</b>	2.430(3)			
<b>d (S1-S1) (Å)</b>	3.306(3)			
<b>d (S1-S2) (Å)</b>	3.3434(20)	3.438(2)		

**Table S3.** Refined structural parameters of “Cd<sub>1</sub>Mo<sub>6</sub>S<sub>8</sub>” at RT (synchrotron powder X-ray diffraction). All atoms refined isotropically.  $U_{iso}$  are made identical for Mo/Cd and S1/S2.

Atom	Site	Occ.	$x$	$y$	$z$	$U_{iso}$ (Å <sup>2</sup> )
Mo	18f	1	0.8275(3)	0.8423(3)	0.3954(3)	0.0042(6)
S1	18f	1	0.9655(11)	0.6840(9)	0.4114(8)	0.004(2)
S2	6c	1	0	0	0.2271(14)	0.004(2)
Cd1	18f	0.1598(17)	0.644(9)	0.265(2)	0.333(3)	0.0042(6)

Refined stoichiometry: Cd<sub>0.96(1)</sub>Mo<sub>6</sub>S<sub>8</sub>

Space group  $R\bar{3}$ :  $a = 9.4175(3)$  Å,  $c = 10.7420(5)$  Å,  $V = 825.06(5)$  Å<sup>3</sup>

$R_{Bragg} = 2.67\%$ ,  $R_{wp} = 9.15\%$ ,  $R_p = 7.29\%$ ,  $\chi^2 = 1.40$

**Table S4.** Refined structural parameters of “Cd<sub>2</sub>Mo<sub>6</sub>S<sub>8</sub>” at RT (synchrotron powder X-ray diffraction). All atoms refined isotropically.  $U_{iso}$  are made identical for Mo/Cd1/Cd2 and S1/S2.

Atom	Site	Occ.	$x$	$y$	$z$	$U_{iso}$ (Å <sup>2</sup> )
Mo	18f	1	0.8373(10)	0.8482(9)	0.4014(10)	0.0070(18)
S1	18f	1	0.967(4)	0.699(4)	0.396(4)	0.058(13)
S2	6c	1	0	0	0.215(6)	0.058(13)
Cd1	18f	0.167(8)	0.606(8)	0.198(5)	0.353(5)	0.0070(18)
Cd2	18f	0.187(12)	0.503(5)	0.045(5)	0.464(5)	0.0070(18)

Refined stoichiometry: Cd<sub>2.1(1)</sub>Mo<sub>6</sub>S<sub>8</sub>

Space group  $R\bar{3}$ :  $a = 9.8185(5)$  Å,  $c = 10.5649(10)$  Å,  $V = 882.04(10)$  Å<sup>3</sup>

$R_{Bragg} = 3.01\%$ ,  $R_{wp} = 9.15\%$ ,  $R_p = 7.29\%$ ,  $\chi^2 = 1.40$

**Table S5.** Refined structural parameters of “Cd<sub>1</sub>Mo<sub>6</sub>Se<sub>8</sub>” at RT (synchrotron powder X-ray diffraction). All atoms refined isotropically.  $U_{iso}$  are made identical for Se1/Se2.

Atom	Site	Occ.	$x$	$y$	$z$	$U_{iso}$ (Å <sup>2</sup> )
Mo	18 $f$	1	0.8314(9)	0.8465(10)	0.4026(10)	0.013(2)
Se1	18 $f$	1	0.9637(10)	0.6809(10)	0.4080(13)	0.0047(17)
Se2	6 $c$	1	0	0	0.2261(18)	0.0047(17)
Cd1	18 $f$	0.143(5)	0.65(3)	0.261(8)	0.331(11)	0.011(18)

Refined stoichiometry: Cd<sub>0.86(3)</sub>Mo<sub>6</sub>Se<sub>8</sub>

Space group  $R\bar{3}$ :  $a = 9.7901(6)$  Å,  $c = 11.1883(13)$  Å,  $V = 928.69(14)$  Å<sup>3</sup>

$R_{Bragg} = 3.06\%$ ,  $R_{wp} = 7.17\%$ ,  $R_p = 5.50\%$ ,  $\chi^2 = 1.63$

**Table S6.** Refined structural parameters of “Cd<sub>2</sub>Mo<sub>6</sub>Se<sub>8</sub>” at RT (synchrotron powder X-ray diffraction). All atoms refined isotropically.  $U_{iso}$  are made identical for Se1/Se2.

Atom	Site	Occ.	$x$	$y$	$z$	$U_{iso}$ (Å <sup>2</sup> )
Mo	18f	1	0.8431(6)	0.8556(7)	0.4001(8)	0.0111(13)
Se1	18f	1	0.9728(9)	0.6930(11)	0.4009(11)	0.021(2)
Se2	6c	1	0	0	0.2116(15)	0.021(2)
Cd2	18f	0.325(10)	0.518(3)	0.100(2)	0.445(2)	0.063(10)

Refined stoichiometry: Cd<sub>1.95(6)</sub>Mo<sub>6</sub>Se<sub>8</sub>

Space group  $R\bar{3}$ :  $a = 10.2463(3)$  Å,  $c = 10.9461(6)$  Å,  $V = 995.22(7)$  Å<sup>3</sup>

$R_{Bragg} = 2.98\%$ ,  $R_{wp} = 7.17\%$ ,  $R_p = 5.50\%$ ,  $\chi^2 = 1.63$