CORRELATION BETWEEN AO_6 POLYHEDRAL DISTORTION AND NEGATIVE THERMAL EXPANSION IN ORTHORHOMBIC $Y_2Mo_3O_{12}$ AND RELATED MATERIALS

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Supporting Information

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Table S1: Phase transition temperatures of $A_2M_3O_{12}$ compounds

Compounds	Temperature / K
$Al_2Mo_3O_{12}$	475 [15], 473 [16]
$Sc_2Mo_3O_{12}$	178 [7], 282 [16]
$In_2Mo_3O_{12}$	608 [16]
$Cr_2Mo_3O_{12}$	658 [16], 676 [15]
$Fe_2Mo_3O_{12}$	772 [16], 786 [15]
$AlFeMo_3O_{12}$	642 [15]
$AlCrMo_3O_{12}$	557 [15]
$CrFeMo_3O_{12}$	738 [15]
$Al_2W_3O_{12}$	267 [16]
$In_2W_3O_{12}$	525 [16], 523 [30]

Table S2: Range of temperature analyzed to determine the thermal expansion coefficient (Figure 13)

Compounds	Temperature / K
$Al_2W_3O_{12}$	293 - 1073 [29]
$Cr_2Mo_3O_{12}$	693 - 1013 [15]
$Sc_2W_3O_{12}$	10 - 450 [6]
$Y_2W_3O_{12}$	293 - 1073 [29]
$Y_2Mo_3O_{12}$	20 - 450 [This work]

Table S3: Atom positions for $Y_2Mo_3O_{12}$ at T = 20, 300 and 450 K.

Atom	x	y	z
		20 K	
Y1	0.38127(7)	0.24881(12)	0.46655(9)
Mo1	0	0.47236(14)	0.25
Mo2	0.35605(7)	0.39486(10)	0.11785(9)
O1	0.14048(44)	0.06426(59)	0.08757(57)
O2	0.05752(41)	0.37229(62)	0.13695(62)
O3	0.26855(42)	0.32576(62)	0.02169(63)
O4	0.41652(46)	0.07438(63)	0.33338(57)
O5	0.46528(42)	0.33051(62)	0.07383(56)
O6	0.33147(45)	0.36206(59)	0.27939(61)
		300 K	
Y1	0.38132(6)	0.24939(9)	0.46757(8)
Mo1	0	0.47191(12)	0.25
Mo2	0.35646(5)	0.39209(8)	0.11441(8)
O1	0.14038(30)	0.06271(31)	0.09356(32)
O2	0.06245(22)	0.37435(33)	0.14012(32)
O3	0.26874(23)	0.32438(32)	0.01726(55)
O4	0.41780(40)	0.06982(32)	0.33576(32)
O5	0.46613(22)	0.32615(33)	0.06815(32)
O6	0.33328(39)	0.35977(32)	0.28045(32)
		450 K	
Y1	0.38158(6)	0.24938(11)	0.46766(9)
Mo1	0	0.47114(13)	0.25
Mo2	0.35705(6)	0.39099(9)	0.11282(9)
O1	0.14064(47)	0.05783(65)	0.09071(62)
O2	0.06565(45)	0.37422(67)	0.14399(63)
O3	0.26680(48)	0.31999(66)	0.01938(66)
O4	0.41701(49)	0.06714(67)	0.33676(62)
O5	0.46706(46)	0.32745(67)	0.06400(62)
O6	0.33632(48)	0.35410(65)	0.27750(65)

Figure S4: Isotropic displacement factors for Y, Mo1, Mo2 and O.

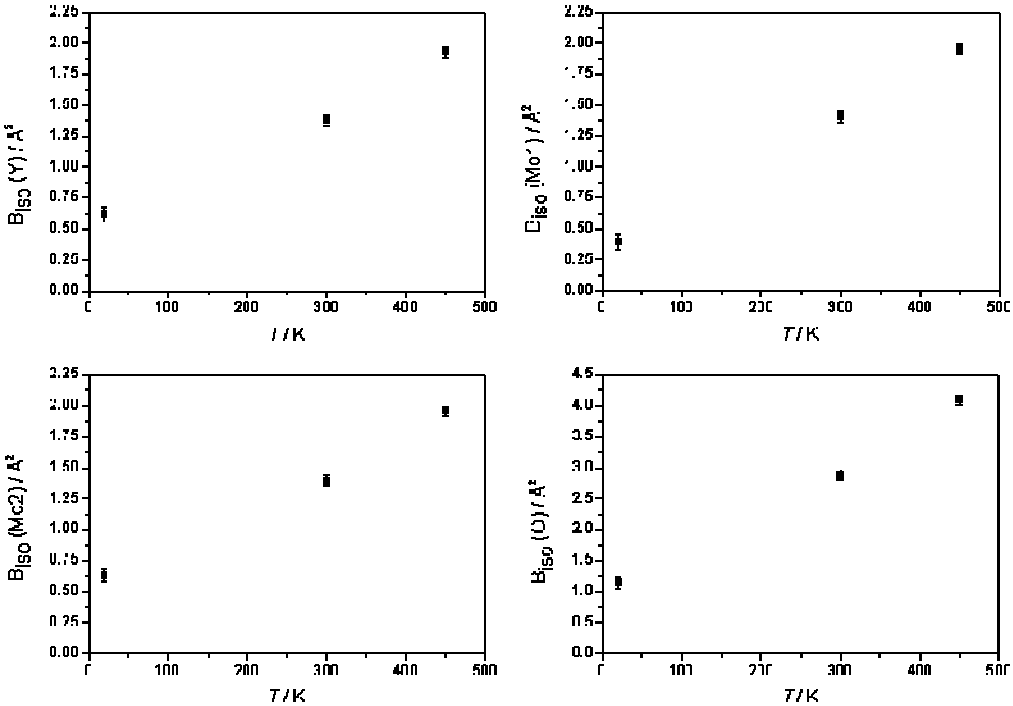


Figure S5: High-resolution XRPD pattern for $Y_2Mo_3O_{12}$ at $T = 20$ K. Experimental profile (points), calculated and difference profile (full lines).

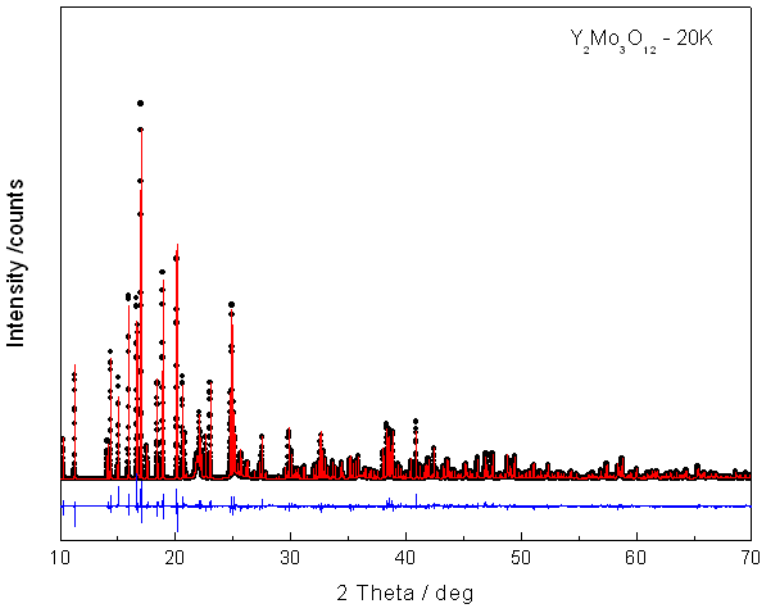


Figure S6: High-resolution XRPD pattern for $Y_2Mo_3O_{12}$ at $T = 450$ K. Experimental profile (points), calculated and difference profile (full lines).

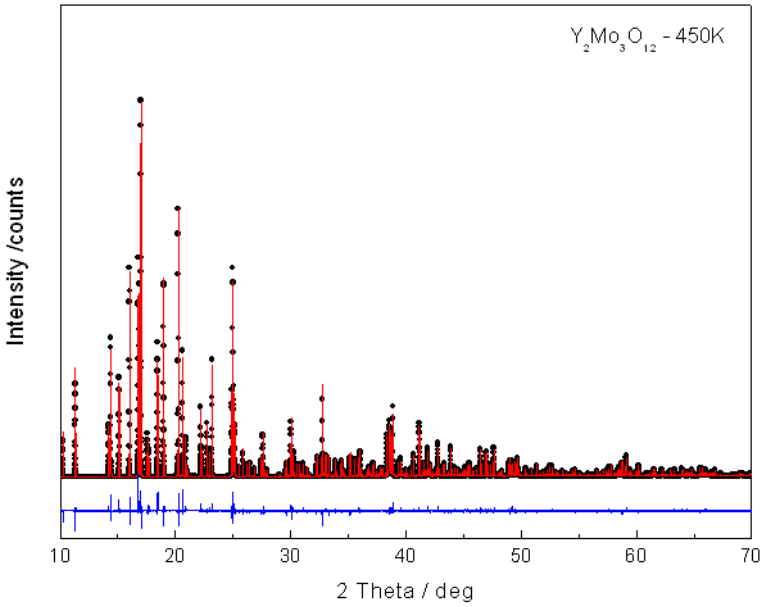


Figure S7: Volume distortion parameter (υ) of ZrO_6 polyhedral as a function of temperature for ZrW_2O_8.

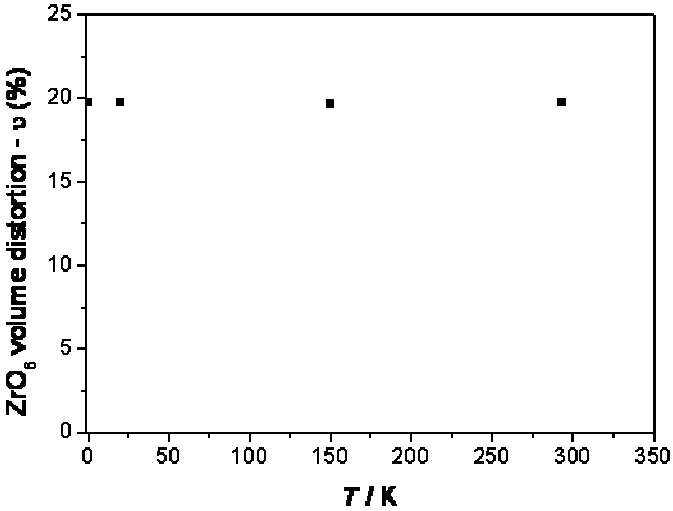


Figure S8: Calculated valences for Y^{3+}, W^{6+}, O^{2-} as a function of temperature for $Y_2W_3O_{12}$: Y(■), W1(▲), W2(△), O1(▼), O2(◇), O3(□), O4(▽), O5(○) and O6 (●).

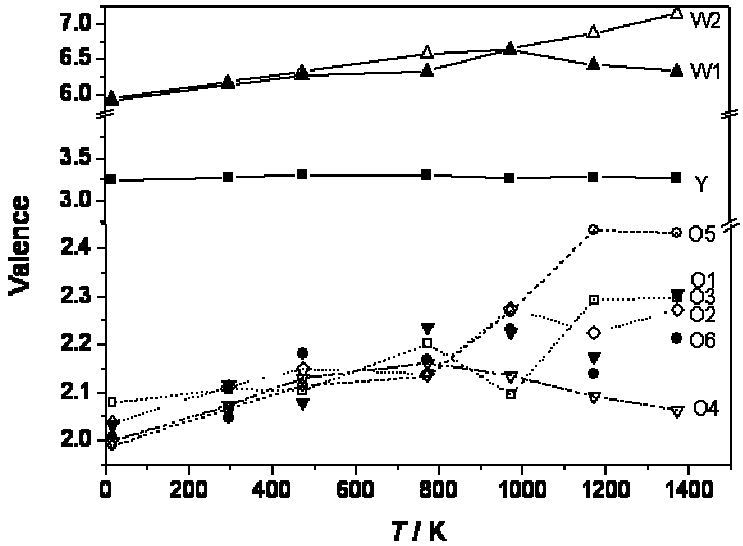


Figure S9: Temperature of the orthorhombic to monoclinic phase transitions in $A_2Mo_3O_{12}$ as a function of the electronegativity of A^{3+} ions (Li-Xue scale). Note that on this scale the electronegativity of Y^{3+} is 1.34.

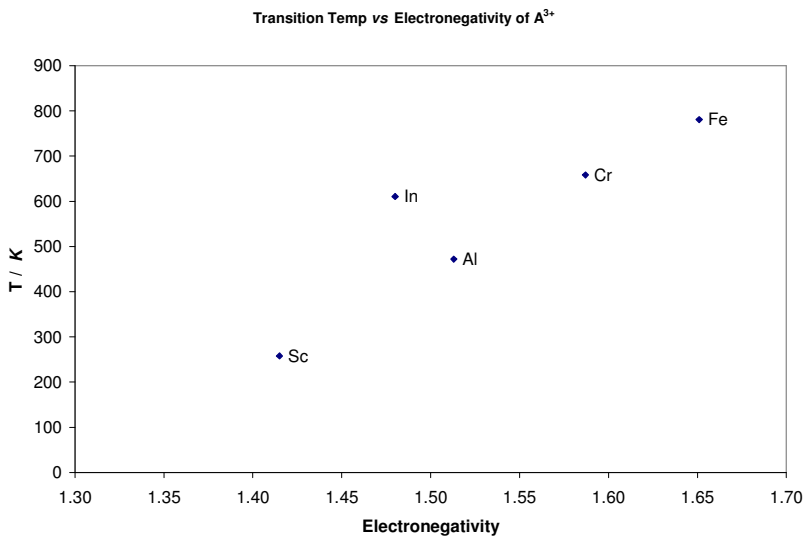


Figure S10: Apparent individual Y-O bond distances as a function of temperature.

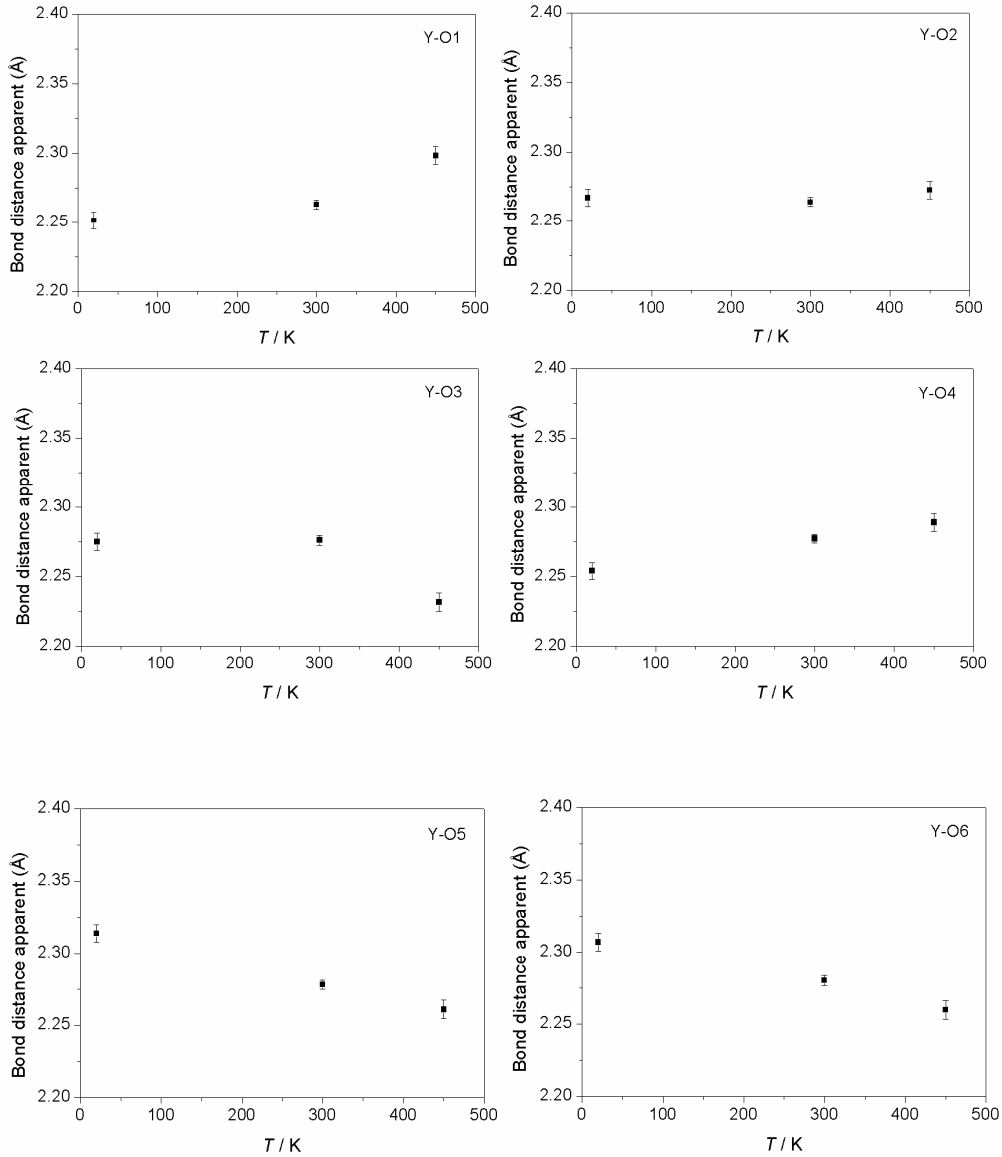


Figure S11: Apparent individual Mo1-O bond distances as a function of temperature.

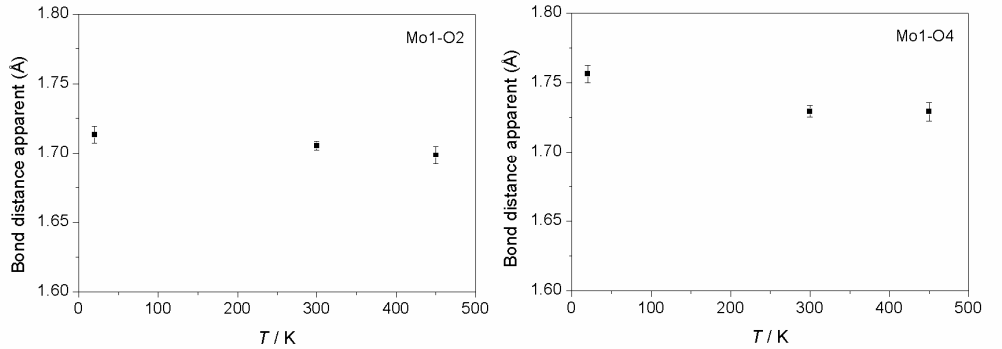
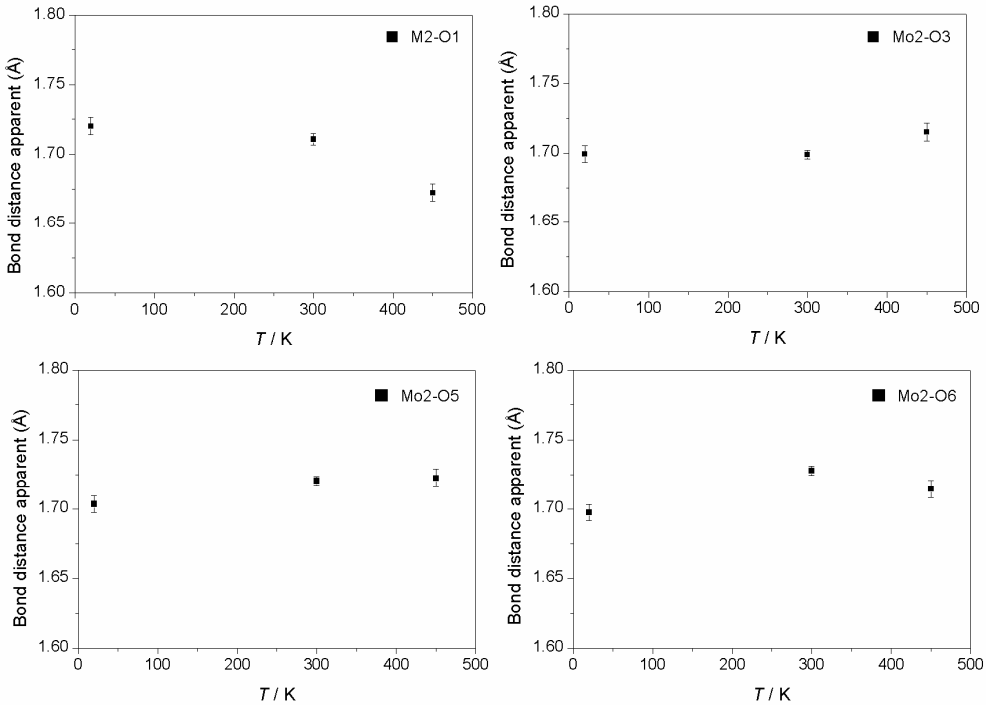


Figure S12: Apparent individual Mo2-O bond distances as a function of temperature.



Experimental Heat Capacity of $Y_2Mo_3O_{12}$

Table S13: Data given in order of measurement; sample mass and thermal contact grease as indicated: m = 4.9491 mg - Apiezon H grease

T / K	C_p / J K^{-1} mol^{-1}	T / K	C_p / J K^{-1} mol^{-1}
391.347	305.5	261.603	289.5
390.873	302.6	261.608	288.7
390.869	302.5	270.467	290.9
381.3	303.1	270.319	290
381.429	305.8	270.322	289.8
381.497	303.1	279.719	294.6
371.969	301.8	279.86	291.6
372.081	303.4	279.862	291.3
372.128	304.3	289.18	294.2
362.635	301.4	289.307	293
362.729	303.3	289.323	292.1
362.793	303.3	298.864	297.4
353.34	300.1	299.001	295.5
353.434	300.6	299.005	295.5
353.473	302.4	308.425	299.9
345.385	302.5	308.562	297.2
345.577	300.9	308.567	296.3
345.588	300.4	318.03	297.6
336.513	302.6	318.016	292.4
336.717	301.1	318.022	297.7
336.706	302.1	327.535	302
252.618	282.5	327.669	300.1
252.268	283.3	327.676	299.6
252.225	283.6	continued…	
261.426	296.5		

Table S14: Data given in order of measurement; sample mass and thermal contact grease as indicated: m = 11.4947 mg - Apiezon T grease

T / K	C_p/ J K^{-1} mol^{-1}	T / K	C_p/ J K^{-1} mol^{-1}	T / K	C_p/ J K^{-1} mol^{-1}
199.328	263.6	9.122	4.493	9.781	5.472
199.266	264.1	9.106	4.461	9.803	5.447
199.216	264.4	9.108	4.46	9.798	5.48
157.443	234.8	7.218	2.303	12.642	10.16
157.327	235.4	7.194	2.274	12.643	10.14
157.29	235.8	7.189	2.27	12.642	10.15
124.396	202.5	5.562	0.983	16.235	17.13
124.171	203.1	5.56	0.985	16.227	17.18
124.121	203.3	5.562	0.985	16.23	17.19
98.105	169.8	4.379	0.417	20.775	26.88
98.017	170.2	4.38	0.418	20.821	27.15
97.943	170.5	4.382	0.42	20.829	27.28
77.755	138.4	3.481	0.173	26.679	40.44
77.34	137.8	3.482	0.173	26.744	40.52
77.277	138	3.483	0.173	26.751	40.61
61.33	108.7	2.751	0.0704	34.246	57.03
61.016	108.3	2.753	0.0698	34.342	57.08
60.97	108.4	2.753	0.0699	34.347	57.01
48.342	84.69	2.191	0.0309	43.924	76.96
48.108	84.44	2.192	0.0311	44.06	77.05
48.086	84.45	2.193	0.0311	44.078	76.92
38.101	64.36	2.212	0.0324	56.326	101.1
37.926	64.08	2.213	0.0321	56.517	101.2
37.903	64.2	2.213	0.0322	56.541	101.1
29.998	47.34	2.815	0.0769	72.22	129.8
29.886	47.2	2.815	0.0768	72.472	130
29.875	47.37	2.816	0.0764	72.51	129.8
23.62	33.23	3.598	0.198	92.657	165.6
23.559	33.17	3.599	0.198	92.915	165.6
23.543	33.14	3.601	0.198	92.978	165.3
18.589	22.21	4.612	0.51	118.993	199.8
18.576	22.36	4.614	0.509	119.268	199.5
18.545	22.04	4.615	0.513	119.337	198.9
14.586	14.04	5.92	1.23	152.779	234.4
14.595	13.99	5.922	1.234	153.05	233.5
14.616	13.99	5.926	1.235	153.118	233
11.548	8.282	7.605	2.693	196.247	265.2
11.542	8.218	7.61	2.693	196.499	263.1
11.543	8.219	7.614	2.697	196.543	262.6

Table S15: Data given in order of measurement; sample mass and thermal contact grease as indicated: m = 11.4947 mg - Apiezon T grease (second loading)

T / K	C_p/ J K^{-1} mol^{-1}
215.02	275.2
215.096	274.6
215.074	274.5
207.08	272.1
207.15	271.5
207.13	271.6
199.152	269.4
199.22	268.9
199.193	268.9
191.205	265.1
191.265	264.4
191.24	264.6
183.27	260.3
183.311	260.4
183.294	260.4
175.321	254.5
175.347	254.9
175.332	254.4
167.373	248
167.388	248.1
167.371	248.2
159.43	241.2
159.436	241.3
159.42	241.8
151.487	234.5
151.48	234.7
151.462	234.5

Table S16: Data given in order of measurement; sample mass and thermal contact grease as indicated: m = 13.9403 mg - Apiezon H grease

T / K	C_p/ J K^{-1} mol^{-1}	T / K	C_p/ J K^{-1} mol^{-1}
390.372	308	297.42	296.8
390.385	307.4	297.588	296.3
390.384	306.9	297.576	295.8
380.688	307.2	287.905	294.4
380.831	307.8	288.066	293.2
380.894	306.7	288.049	293.3
371.221	304.6	278.387	290.7
371.336	305.8	278.54	289.7
371.404	305.7	278.517	289.9
361.792	303.9	268.875	287.7
361.878	305.7	269.016	287.3
361.941	304.6	268.997	287.1
352.35	302.5	259.362	284.7
352.478	303.1	259.495	284.4
352.525	303	259.474	284.3
344.531	302.8	249.86	283.5
344.718	301.9	249.975	283.1
344.718	301.4	247.329	282.7
335.443	301.9	247.054	282.1
335.641	301.2	247.051	281.9
335.626	301.4	235.248	279.7
325.947	300.4	235.326	279.5
326.133	299.5	235.308	279.4
326.116	300	223.543	274.8
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Crystallographic information files (CIF) at 20, 300 and 450K

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Mo2 Mo6+ 8 d 0.35646(5) 0.39209(8) 0.11441(8) 1 1.398(41)
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O4 O2- 8 d 0.41780(40) 0.06982(32) 0.33576(32) 1 2.877(75)
O5 O2- 8 d 0.46613(22) 0.32615(33) 0.06815(32) 1 2.877(75)
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_publ_contact_author_address 'Marqu\^es de S\~ao Vicente 225'
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'Ferreira F. F.' 'LNLS, Brazil'
'White M. A.' 'Dalhousie University, Canada'
'Miller K.' 'Dalhousie University, Canada'
'Johnson M. B.' 'Dalhousie University, Canada'

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Mo1 Mo6+ 4 c 0 0.47113(13) 0.25 1 1.960(38)
Mo2 Mo6+ 8 d 0.357047(63) 0.390995(93) 0.112818(89) 1 1.960(38)
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