Electronic Supplementary Information

Crystal Structures and Phase Transition Behaviour in the 5d transition metal oxides $A\mathrm{ReO_4}$ (A = Ag, Na, K, Rb, Cs and Tl).

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Table S1: Atomic coordinates and ADPs derived from Rietveld refinements against neutron diffraction data for the AReO$_4$ oxides. The temperatures used for TlReO$_4$ are indicated; all other data were measured for the samples at room temperature.

Sample	Atom	x	y	z	U_{iso} / Å^2
NaReO$_4$	a = 5.3725(1) c = 11.7412(4) Å Vol = 338.90(2) Å^3				
$I4_1/a$ (No. 88)	Na	0	¼	$^5/_8$	0.0344(11)
χ^2 = 5.905	Re	0	¼	$^1/_8$	0.0081(3)
R_p 0.0798 R_{wp} 0.0596	O	0.1274(3)	0.0154(3)	0.2076(1)	0.0209(3)
AgReO$_4$	a = 5.37674(7) c = 11.8006(2) Å Vol = 341.15(1) Å^3				
$I4_1/a$ (No. 88)	Ag	0	¼	$^5/_8$	0.0205(5)
χ^2 = 2.31	Re	0	¼	$^1/_8$	0.0094(3)
R_p 0.0609 R_{wp} 0.0486	O	0.1312(2)	0.0195(2)	0.2080(1)	0.0196(3)
KReO$_4$	a = 5.67625(8) c = 12.6994(4) Å Vol = 409.17(1) Å^3				
$I4_1/a$ (No. 88)	K	0	¼	$^5/_8$	0.0201(8)
χ^2 = 2.36	Re	0	¼	$^1/_8$	0.0124(3)
R_p 0.0635 R_{wp} 0.0502	O	0.1162(3)	0.0296(2)	0.2026(1)	0.0250(3)
TlReO$_4$ 50 K	a = 5.78654(9) c = 12.8718(3) Å Vol = 431.00(2) Å^3				
$I4_1/a$ (No. 88)	Tl	0	¼	$^5/_8$	0.0048(3)
χ^2 = 2.70	Re	0	¼	$^1/_8$	0.0026(4)
R_p 0.0609 R_{wp} 0.0486	O	0.1192(3)	0.0355(3)	0.2013(1)	0.0100(3)
TlReO$_4$ 450 K	a = 5.7710(3) c = 13.4041(3) Å Vol = 447.34(5) Å^3				
$I4_1/a$ (No. 88)	Tl	0	¼	$^5/_8$	0.0453(12
χ^2 = 2.51	Re	0	¼	$^1/_8$	0.0330(11)
R_p 0.0525 R_{wp} 0.0417	O	0.0875(6)	0.0251(6)	0.1981(3)	0.0779(11)
RbReO$_4$	a = 5.8329(1) c = 13.2543(3) Å Vol = 450.94(2) Å^3				
$I4_1/a$ (No. 88)	Rb	0	¼	$^5/_8$	0.0225(6)
χ^2 = 2.51	Re	0	¼	$^1/_8$	0.0182(5)
R_p 0.0544 R_{wp} 0.0423	O	0.1048(3)	0.0329(3)	0.1992(2)	0.0337(4)
CsReO$_4$	a = 5.7476(3) b = 5.9881(3) c = 14.2928(7) Å Vol = 491.91(5) Å^3				
Pnma (No. 62)	Cs	0.0230(9)	¾	0.1276(4)	0.0276(12)
χ^2 = 2.02	Re	0.0392(5)	¼	0.3800(2)	0.0196(7)
R_p 0.0547 R_{wp} 0.0433	O1	0.822(1)	¼	0.0830(3)	0.0355(13)
	O2	0.8552(9)	¼	0.4752(4)	0.0640(19)
	O3	0.0105(9)	0.5153(6)	0.6857(2)	0.0498(12)

Table S2: Atomic coordinates and ADPs derived from Rietveld refinements against neutron diffraction data collected at room temperature on $TlReO_4$ oxide.

a = 17.4071(8) b = 13.3329(5) c = 5.62872(28) Å β= 90.156(5)^0 Vol = 1306.34(10) Å^3

Name	x	y	z	Ui *100 Å^2
Tl1	0.0820(11)	0.3747(10)	0.4814(24)	2.54(24)
Tl2	0.2450(10)	0.6349(10)	0.4811(23)	2.92(38)
Tl3	0.4104(10)	0.3767(10)	0.4962(25)	2.51(33)
Re1	0.2492(8)	0.3792(12)	-0.0194(24)	2.77(38)
Re2	0.4181(9)	0.6269(8)	0.0041(20)	1.42(24)
Re3	0.0845(9)	0.6157(9)	0.0317(17)	1.67(26)
O11	0.2769(12)	0.4571(15)	-0.2414(39)	3.66(55)
O12	0.2095(12)	0.4433(14)	0.2268(34)	2.52(47)
O13	0.1866(12)	0.2921(15)	-0.1226(32)	3.00(49)
O14	0.3262(15)	0.3045(21)	0.0610(50)	5.11(73)
O21	0.3803(12)	0.5515(16)	0.2114(44)	3.76(58)
O22	0.4579(18)	0.5525(26)	-0.2091(67)	9.03(120)
O23	0.4866(14)	0.6991(24)	0.1190(42)	3.58(56)
O24	0.3448(14)	0.6980(21)	-0.1330(45)	3.94(61)
O31	0.1704(11)	0.6678(14)	-0.0132(34)	3.62(49)
O32	0.0031(11)	0.6915(13)	-0.0513(32)	1.59(38)
O33	0.0752(10)	0.5807(11)	0.3215(26)	2.32(30)
O34	0.0802(14)	0.5078(11)	-0.1322(25)	3.58(38)

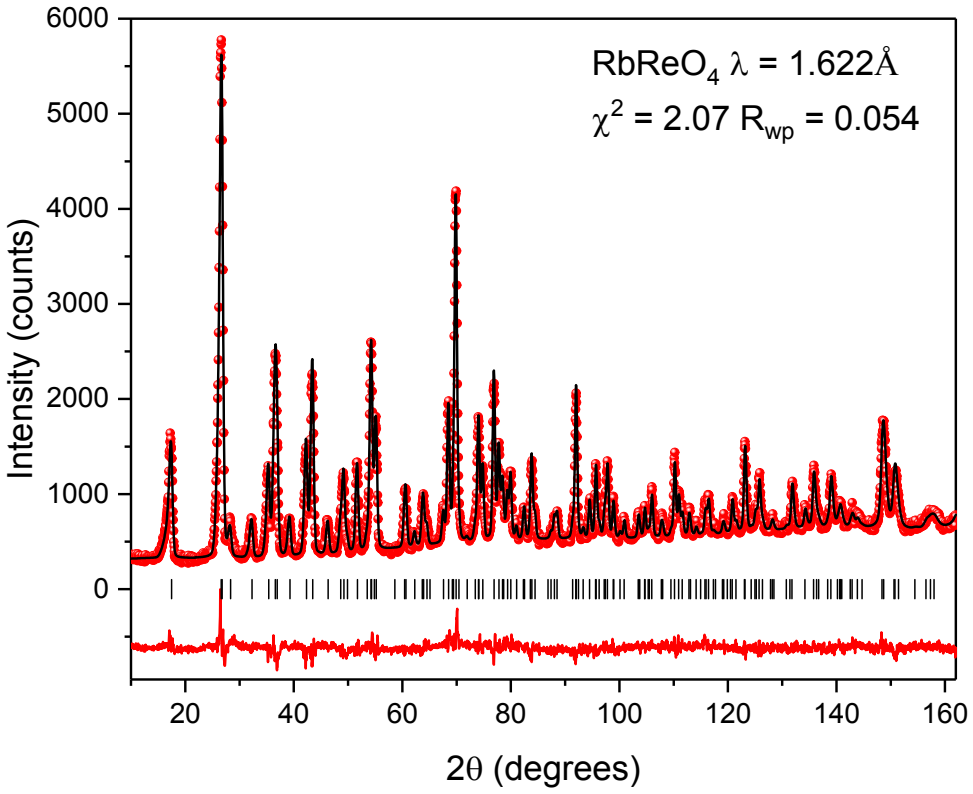

Figure S1(a). Observed (red symbols) calculated (black line) and difference (red line) neutron diffraction profiles for $RbReO_4$ measured at room temperature and fitted in space group $I4_1/a$. The short vertical lines show the positions of the space group allowed Bragg reflections.

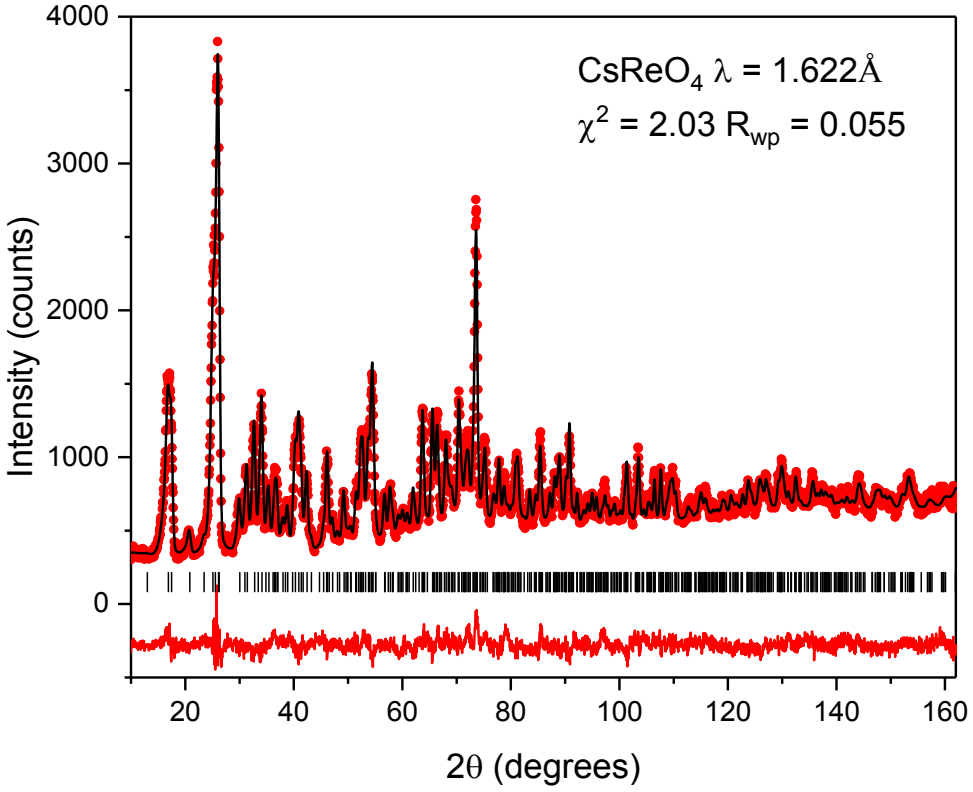

Figure S1(b). Observed (red symbols) calculated (black line) and difference (red line) neutron diffraction profiles for $CsReO_4$ measured at room temperature and fitted in space group *Pnma*. The short vertical lines show the positions of the space group allowed Bragg reflections.

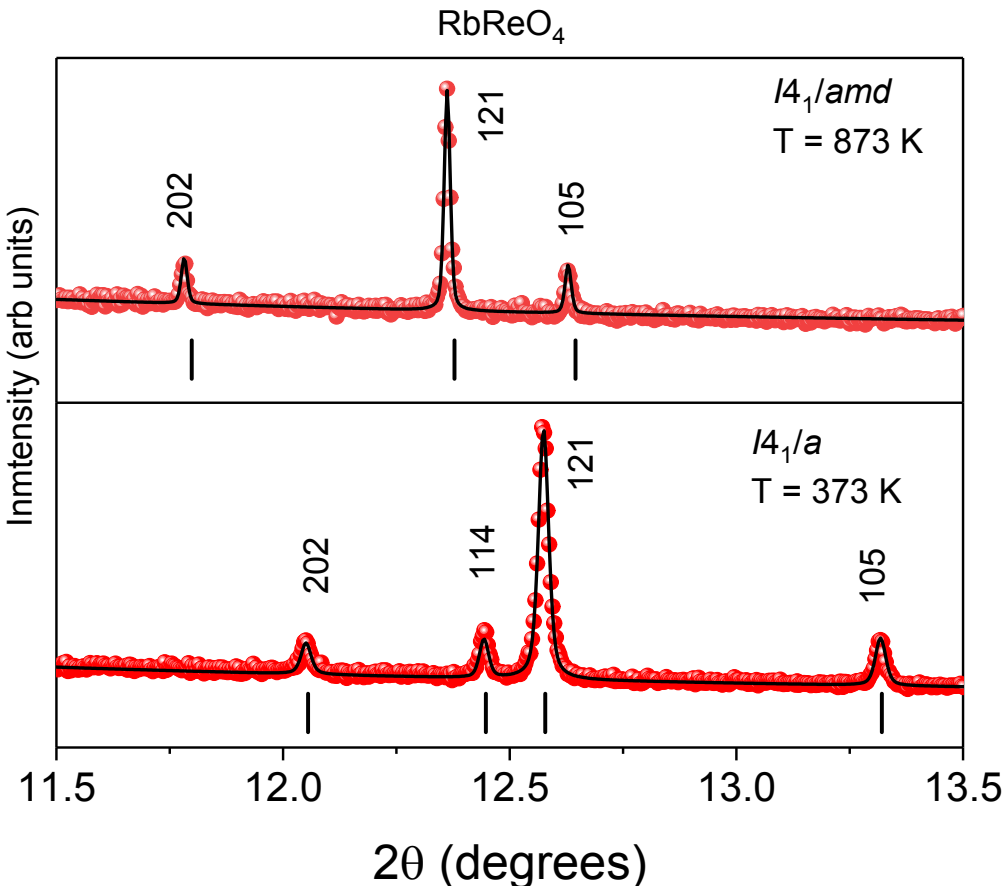

Figure S2 Portions of the SXRD profiles for $RbReO_4$illustrating the loss of the (114) reflection indicative of the transition from $I4_1/a$ to $I4_1/amd$.

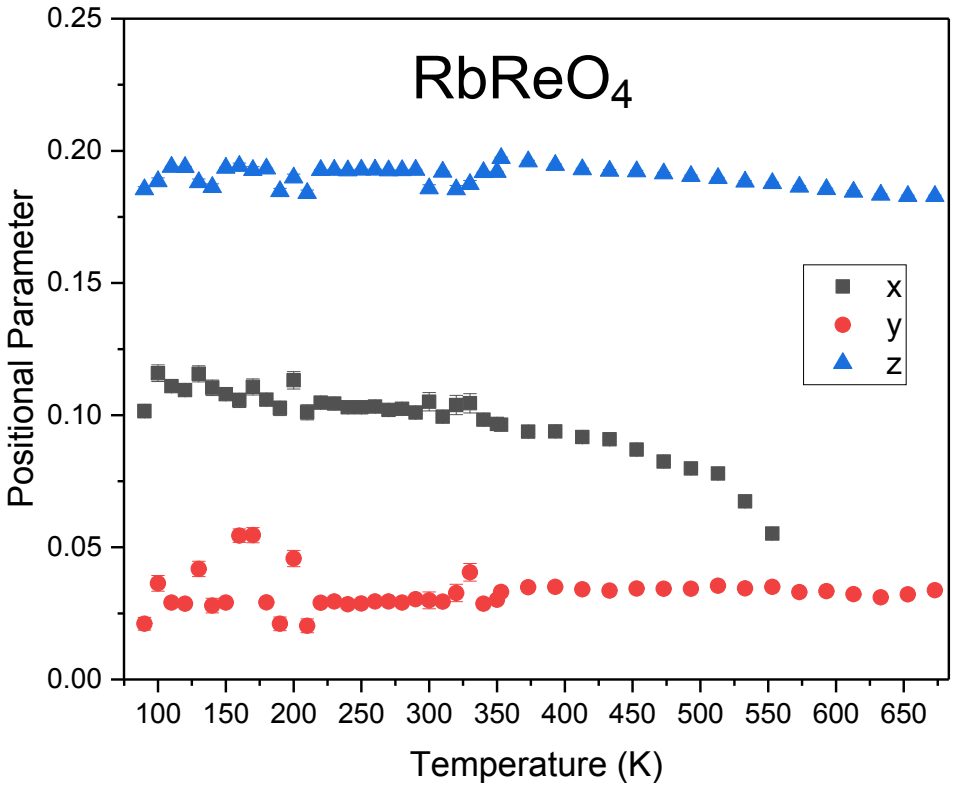

Figure S3. Temperature dependence of the refined oxygen positional parameters for $ReReO_4$ established by Rietveld refinement against synchrotron X-ray diffraction data. The x value is required to be zero in space group $I4_1/amd$.

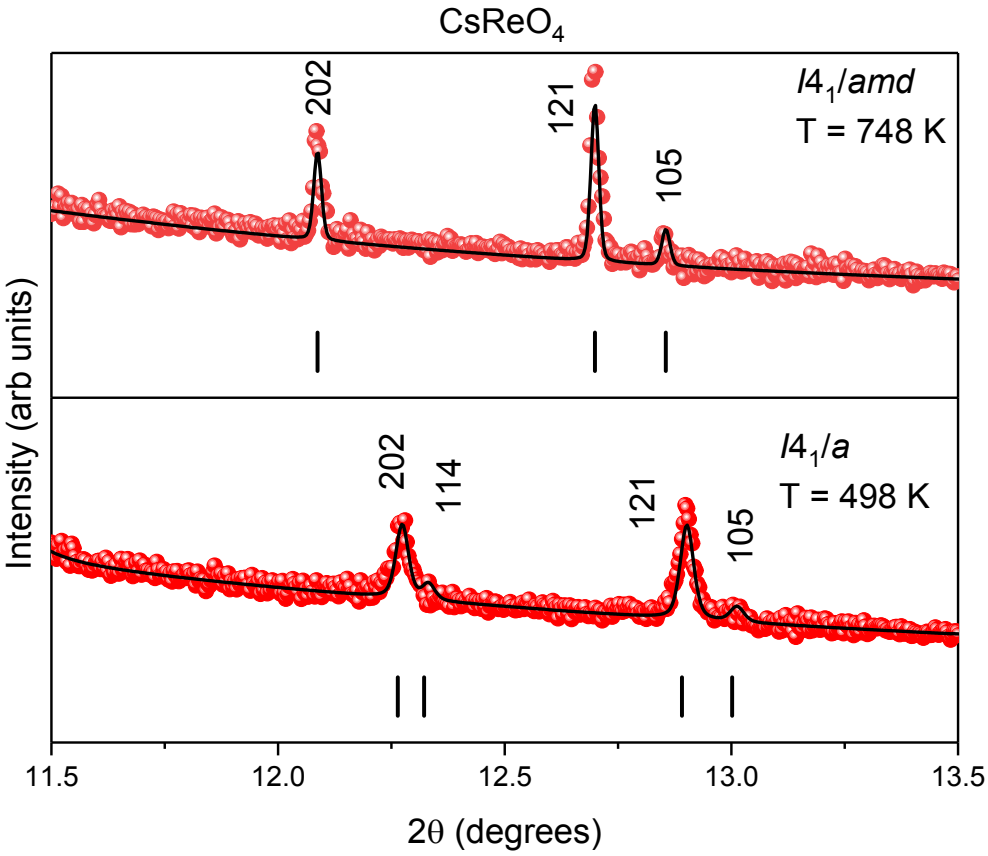

Figure S4 Portions of the SXRD profiles for $CsReO_4$ illustrating the loss of the (114) reflection indicative of the transition from $I4_1/a$ to $I4_1/amd$.

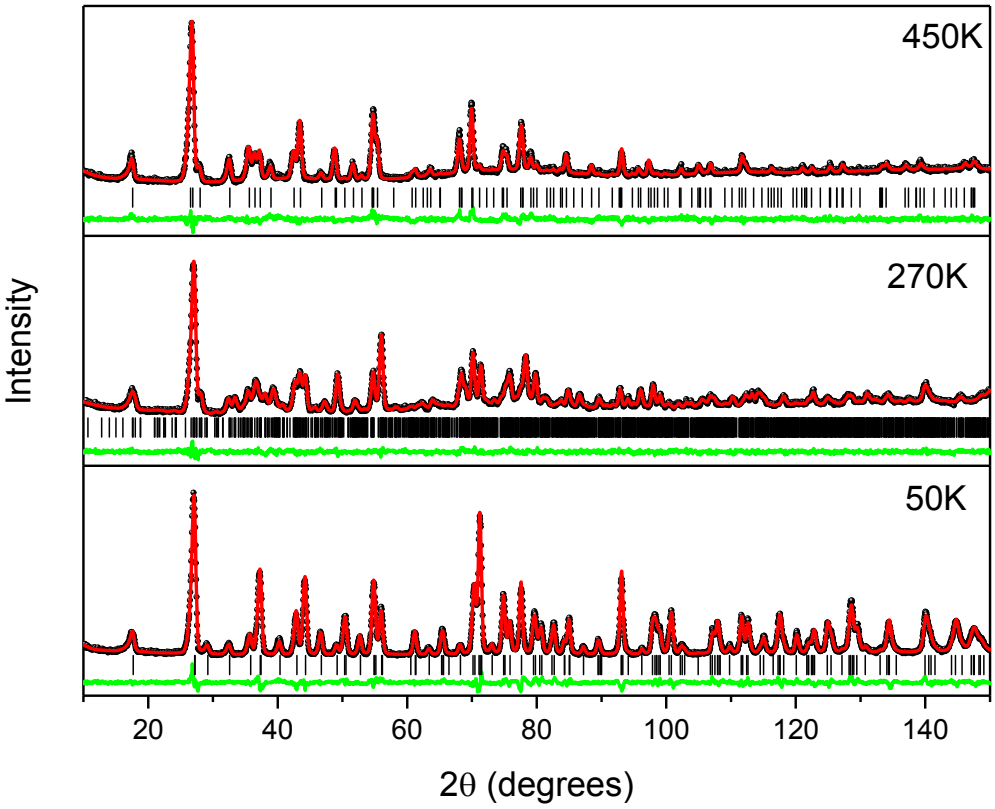

Figure S5 Rietveld fits for $TlReO_4$ at selected temperatures.

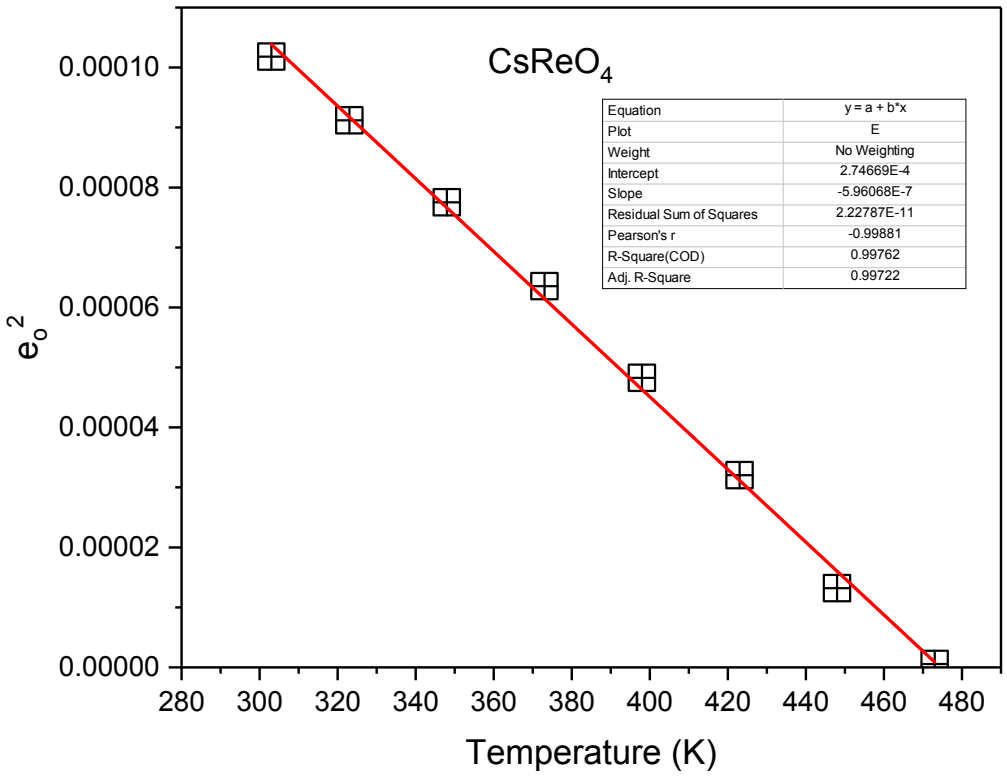

Figure S6. Temperature dependence of the square of the spontaneous strain for $CsReO_4$ showing the continuous transition to be second order.