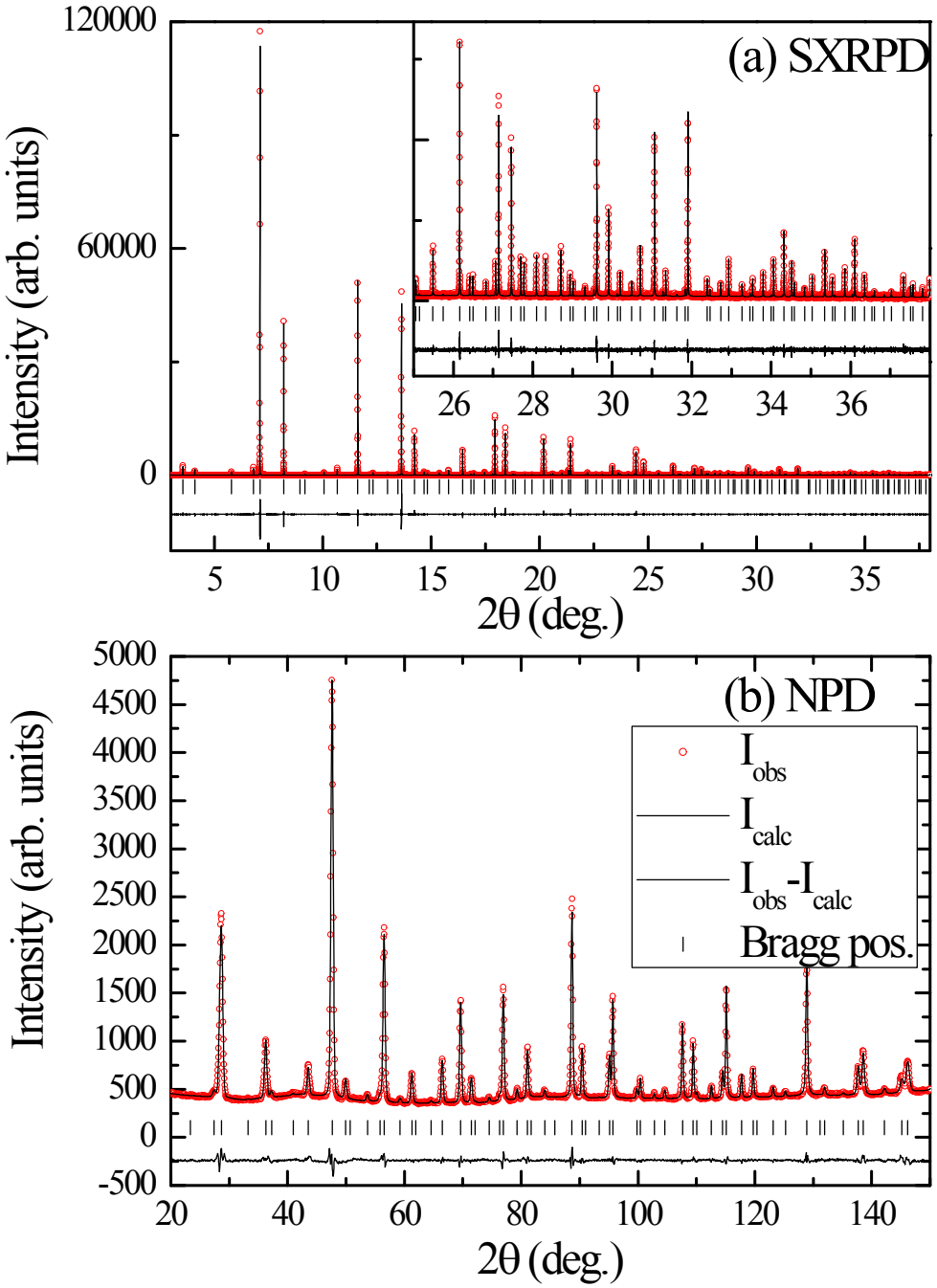

Fig S1 Rietveld refinement of SXRPD and NPD data corresponding to LWO sample using $Fm\bar{3}m$ SG (same data as publication[1], same description as in publication[2]).

[1] A. Magrasó, J. M. Polfus, C. Frontera, J. Canales-Vazquez, L.-E. Kalland, C. H. Hervoches, S. Erdal, R. Hancke, M. S. Islam, T. Norby and R. Haugsrud, J. Mater. Chem., 2012, 22(5), 1762–1764
[2] T. Scherb, S. A. J. Kimber, C. Stephan, P. F. Henry, G. Schumacher, J. Just, S. Escolastico, J. M. Serra, J. Seeger, A. H. Hill and J. Banhart, arXiv:1305.3385v1, 2013

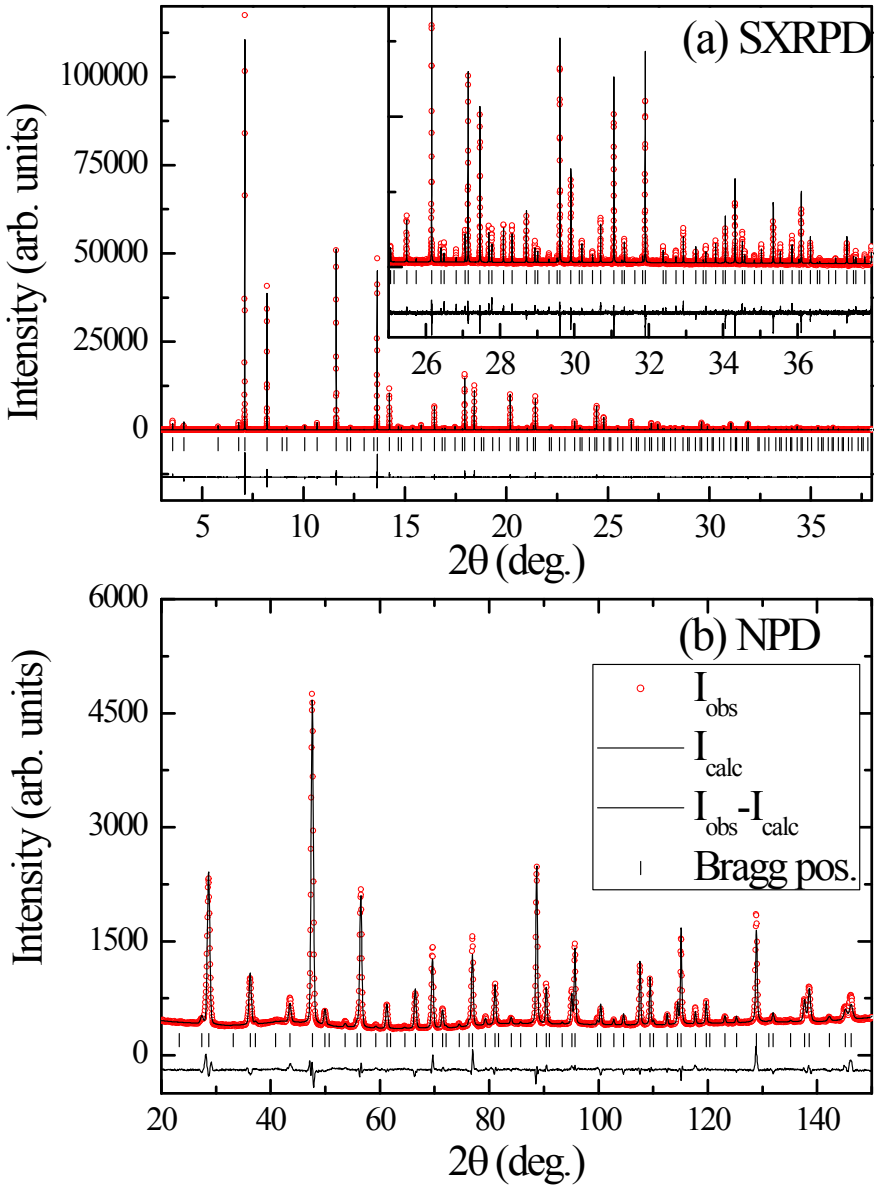

Fig. S2 Rietveld refinement of SXRPD and NPD data corresponding to LWO sample using $F\bar{4}3m$ SG (same data as publication[1] and the same description as publication[3], for better comparison)

[3] A. Magraso, C. Frontera, D. Marrero-Lopez and P.Nuñez, Dalton Trans., 2009, 10273–10283

Table S1. Structural details of LWO sample obtained through the joint refinement of SXRPD and NPD data using $F\bar{4}3m$ space group with lattice parameter a=11.17664(6)Å. La1 is placed at 4a (0 0 0), and La2 at 24g (x ¼ ¼); W1 is at 4b (½ ½ ½), and W2 at 4d (¾ ¾ ¾); oxygen ions are all at 16e (x x x) positions. The different parameters, agreement factors, and some relevant bond distances are listed.

La1	B_{iso} (Å^2)	1.5(1)	**O1a**	x	0.132(1)
La2	x	-0.0028(6)		B_{iso}(Å^2)	1.2(1)
	Occ.	0.936	**O1b**	x	0.865(1)
	B_{iso}(Å^2)	2.2(2)		B_{iso}(Å^2)	1.2(1)
W1	B_{iso}(Å^2)	1.04(9)	**O2a**	x	0.409(3)
W2	Occ.	0.064		Occ.	0.74(2)
	B_{iso}(Å^2)	2.2(1)		B_{iso}(Å^2)	5.2(6)
			O2b	x	0.602(3)
				Occ.	0.74(2)
				B_{iso}(Å^2)	5.2(6)
χ^2	SXRPD	1.97	χ^2	NPD	8.59
R_B	SXRPD	4.81	R_B	NPD	7.83
R_{exp}	SXRPD	14.38	R_{exp}	NPD	4.74
R_{wp}	SXRPD	20.2	R_{wp}	NPD	13.9
$d_{La1\text{-}O1a}$ (Å)		2.548(6)	$d_{La2/W2\text{-}O1a}$ (Å)		2.362(6)
$d_{La1\text{-}O1b}$ (Å)		2.621(4)	$d_{La2/W2\text{-}O1b}$ (Å)		2.379(5)
$\langle d_{La1\text{-}O}\rangle$ (Å)		2.584(5)	$d_{La2/W2\text{-}O2a}$ (Å)		2.697(10)
$d_{W1\text{-}O2a}$ (Å)		1.767(10)	$d_{La2/W2\text{-}O2b}$ (Å)		2.616(11)
$d_{W1\text{-}O2b}$ (Å)		1.973(11)	$\langle d_{La2/W2\text{-}O}\rangle$ (Å)		2.513(9)
$\langle d_{W1\text{-}O}\rangle$ (Å)		1.870(11)			

Table S2: Comparison of the positions of oxygen anions obtained by DFT with those from diffraction in the disorder model $Fm\bar{3}m$. Last column prints the distance between both positions. Those marked in bold and italic correspond to oxygen ions surrounding, in DFT structure, a W cation placed in La2/W2 positions.

	x-DFT	y-DFT	z-DFT	x-diff.	y-diff.	z-diff.	Dist(Å)
O1 O	0.12462	0.12909	0.07164	0.13342	0.13342	0.06671	0.15551
O2 O	0.87098	0.87228	0.06734	0.86658	0.86658	0.06671	0.08174
O3 O	0.87165	0.13884	0.43339	0.86658	0.13342	0.43329	0.08302
O4 O	0.13478	0.87403	0.43485	0.13342	0.86658	0.43329	0.09159
O5 O	0.13216	0.63261	0.31738	0.13342	0.63342	0.31671	0.02247
O6 O	0.87215	0.37938	0.3183	0.86658	0.36658	0.31671	0.16009
O7 O	0.87601	0.6419	0.18177	0.86658	0.63342	0.18329	0.14583
O8 O	*0.18685*	*0.33839*	*0.18471*	*0.13342*	*0.36658*	*0.18329*	*0.67625*
O9 O	0.62748	0.14121	0.31325	0.63342	0.13342	0.31671	0.13411
O10 O	0.37457	0.8783	0.31389	0.36658	0.86658	0.31671	0.17069
O11 O	*0.35795*	*0.16401*	*0.19253*	*0.36658*	*0.13342*	*0.18329*	*0.41111*
O12 O	0.63346	0.879	0.1816	0.63342	0.86658	0.18329	0.14393
O13 O	0.63547	0.63855	0.07181	0.63342	0.63342	0.06671	0.12971
O14 O	0.3709	0.37215	0.05675	0.36658	0.36658	0.06671	0.23628
O15 O	0.3589	0.63626	0.4282	0.36658	0.63342	0.43329	0.14609
O16 O	0.6296	0.36463	0.43289	0.63342	0.36658	0.43329	0.04879
O17 O	0.86447	0.87712	0.43222	0.86658	0.86658	0.43329	0.12255
O18 O	0.13178	0.14085	0.43277	0.13342	0.13342	0.43329	0.08587
O19 O	0.14751	0.872	0.0658	0.13342	0.86658	0.06671	0.17003
O20 O	0.86623	0.15237	0.06766	0.86658	0.13342	0.06671	0.21299
O21 O	0.87517	0.37221	0.18553	0.86658	0.36658	0.18329	0.12529
O22 O	0.13544	0.62562	0.18476	0.13342	0.63342	0.18329	0.09591
O23 O	*0.15425*	*0.32772*	*0.30511*	*0.13342*	*0.36658*	*0.31671*	*0.5571*
O24 O	0.86108	0.63807	0.31348	0.86658	0.63342	0.31671	0.10818
O25 O	0.36667	0.87172	0.18325	0.36658	0.86658	0.18329	0.05749
O26 O	0.63136	0.13944	0.18312	0.63342	0.13342	0.18329	0.07125
O27 O	0.63715	0.87222	0.31542	0.63342	0.86658	0.31671	0.08093
O28 O	*0.33225*	*0.15469*	*0.31097*	*0.36658*	*0.13342*	*0.31671*	*0.46947*
O29 O	0.37173	0.37466	0.4292	0.36658	0.36658	0.43329	0.14087
O30 O	0.63705	0.63884	0.43352	0.63342	0.63342	0.43329	0.07312
O31 O	0.64368	0.38017	0.06512	0.63342	0.36658	0.06671	0.1937
O32 O	0.37495	0.64718	0.06501	0.36658	0.63342	0.06671	0.18406
O33 O	0.61875	0.6202	0.2167	0.61167	0.61167	0.21685	0.124
O34 O	0.60348	0.43252	0.3068	0.61167	0.4337	0.30584	0.09498
O35 O	0.42649	0.60592	0.30069	0.4337	0.61167	0.30584	0.15459
O36 O	0.42834	0.89598	0.44373	0.4337	0.88833	0.44417	0.10491
O37 O	0.584	0.89613	0.0373	0.61167	0.88833	0.03315	0.33459
O38 O	0.38295	0.05937	0.0578	0.38833	0.0663	0.05584	0.10745
O39 O	0.88617	0.39378	0.46979	0.88833	0.38833	0.46685	0.09284
O40 O	0.05145	0.38839	0.06008	0.0663	0.38833	0.05584	0.19122

O41 O	0.88859	0.58412	0.03862	0.88833	0.61167	0.03315	0.33147
O42 O	*0.13016*	*0.12412*	*0.22792*	*0.11167*	*0.11167*	*0.21685*	*0.35131*
O43 O	0.12366	0.93143	0.30781	0.11167	0.9337	0.30584	0.14339
O44 O	0.93849	0.12307	0.30528	0.9337	0.11167	0.30584	0.13883
O45 O	*0.3794*	*0.37504*	*0.26543*	*0.38833*	*0.38833*	*0.28315*	*0.43485*
O46 O	0.40189	0.55832	0.1847	0.38833	0.5663	0.19417	0.27533
O47 O	0.5877	0.39164	0.19149	0.5663	0.38833	0.19417	0.24945
O48 O	0.60107	0.12892	0.04953	0.61167	0.11167	0.03315	0.43063
O49 O	0.38813	0.12416	0.466	0.38833	0.11167	0.46685	0.14097
O50 O	0.61292	0.07467	0.44187	0.61167	0.0663	0.44417	0.10771
O51 O	0.89924	0.8972	0.29152	0.88833	0.88833	0.28315	0.24445
O52 O	0.90425	0.05256	0.19058	0.88833	0.0663	0.19417	0.24848
O53 O	0.08066	0.88953	0.19553	0.0663	0.88833	0.19417	0.16398
O54 O	0.12204	0.60711	0.04771	0.11167	0.61167	0.03315	0.34939
O55 O	0.11568	0.43684	0.43951	0.11167	0.4337	0.44417	0.11876
O56 O	0.93993	0.6176	0.44023	0.9337	0.61167	0.44417	0.13044
O57 O	0.14138	0.13552	0.56799	0.13342	0.13342	0.56671	0.0964
O58 O	0.87013	0.87346	0.56979	0.86658	0.86658	0.56671	0.11063
O59 O	0.87103	0.13806	0.93392	0.86658	0.13342	0.93329	0.07326
O60 O	0.13662	0.87316	0.93308	0.13342	0.86658	0.93329	0.08195
O61 O	0.12852	0.63875	0.81118	0.13342	0.63342	0.81671	0.14781
O62 O	0.87378	0.37931	0.81592	0.86658	0.36658	0.81671	0.16449
O63 O	0.86627	0.64069	0.68588	0.86658	0.63342	0.68329	0.09988
O64 O	*0.17849*	*0.34926*	*0.68504*	*0.13342*	*0.36658*	*0.68329*	*0.54132*
O65 O	0.63411	0.13081	0.81282	0.63342	0.13342	0.81671	0.09208
O66 O	0.36642	0.86351	0.81644	0.36658	0.86658	0.81671	0.0349
O67 O	*0.34715*	*0.15954*	*0.68591*	*0.36658*	*0.13342*	*0.68329*	*0.3687*
O68 O	0.63382	0.87448	0.68216	0.63342	0.86658	0.68329	0.09199
O69 O	0.63664	0.63997	0.56984	0.63342	0.63342	0.56671	0.10752
O70 O	0.36774	0.3724	0.56575	0.36658	0.36658	0.56671	0.06974
O71 O	0.36239	0.60905	0.93394	0.36658	0.63342	0.93329	0.27688
O72 O	0.60716	0.36808	0.93373	0.63342	0.36658	0.93329	0.29428
O73 O	0.8637	0.86531	0.93199	0.86658	0.86658	0.93329	0.04565
O74 O	0.12857	0.13053	0.93499	0.13342	0.13342	0.93329	0.07369
O75 O	0.13455	0.8727	0.56667	0.13342	0.86658	0.56671	0.0696
O76 O	0.86849	0.14632	0.5667	0.86658	0.13342	0.56671	0.14582
O77 O	0.88253	0.37159	0.68263	0.86658	0.36658	0.68329	0.18752
O78 O	0.1376	0.62799	0.68006	0.13342	0.63342	0.68329	0.1053
O79 O	*0.17204*	*0.33287*	*0.80746*	*0.13342*	*0.36658*	*0.81671*	*0.6094*
O80 O	0.86553	0.63742	0.8188	0.86658	0.63342	0.81671	0.06575
O81 O	0.36848	0.87433	0.68561	0.36658	0.86658	0.68329	0.10321
O82 O	0.62666	0.14215	0.68516	0.63342	0.13342	0.68329	0.13035
O83 O	0.62624	0.87116	0.81884	0.63342	0.86658	0.81671	0.10648
O84 O	*0.33936*	*0.15871*	*0.80475*	*0.36658*	*0.13342*	*0.81671*	*0.49412*
O85 O	0.63788	0.64173	0.93463	0.63342	0.63342	0.93329	0.10963

O86 O	0.63606	0.37367	0.56498	0.63342	0.36658	0.56671	0.09302
O87 O	0.374	0.6405	0.56286	0.36658	0.63342	0.56671	0.1434
O88 O	0.60652	0.61243	0.79148	0.61167	0.61167	0.78315	0.19517
O89 O	0.58789	0.38849	0.80734	0.5663	0.38833	0.80584	0.24374
O90 O	0.38267	0.57295	0.80797	0.38833	0.5663	0.80584	0.10865
O91 O	0.4159	0.89793	0.95379	0.4337	0.88833	0.94417	0.31213
O92 O	0.61532	0.89454	0.52983	0.61167	0.88833	0.53315	0.10955
O93 O	0.38817	0.94239	0.55811	0.38833	0.9337	0.55584	0.10965
O94 O	0.89288	0.41597	0.95425	0.88833	0.4337	0.94417	0.30448
O95 O	0.06827	0.39462	0.55765	0.0663	0.38833	0.55584	0.08409
O96 O	0.89581	0.58475	0.55374	0.88833	0.5663	0.55584	0.22752
O97 O	*0.12333*	*0.13513*	*0.72823*	*0.11167*	*0.11167*	*0.71685*	*0.38805*
O98 O	0.10612	0.95581	0.81056	0.11167	0.9337	0.80584	0.27589
O99 O	0.9202	0.12362	0.80637	0.9337	0.11167	0.80584	0.20195
O100 O	*0.38687*	*0.37157*	*0.74042*	*0.38833*	*0.38833*	*0.71685*	*0.55968*
O101 O	0.4402	0.6071	0.69439	0.4337	0.61167	0.69417	0.08898
O102 O	0.60599	0.43397	0.69333	0.61167	0.4337	0.69417	0.0663
O103 O	0.56476	0.12142	0.55812	0.5663	0.11167	0.55584	0.12158
O104 O	0.39096	0.13898	0.94827	0.38833	0.11167	0.96685	0.5165
O105 O	0.61003	0.07111	0.93892	0.61167	0.0663	0.94417	0.13044
O106 O	0.88482	0.89329	0.78405	0.88833	0.88833	0.78315	0.07086
O107 O	0.89282	0.08237	0.69285	0.88833	0.0663	0.69417	0.1889
O108 O	0.06272	0.90556	0.69342	0.0663	0.88833	0.69417	0.19749
O109 O	0.12286	0.61707	0.53063	0.11167	0.61167	0.53315	0.14993
O110 O	0.13355	0.39274	0.95065	0.11167	0.38833	0.96685	0.43994
O111 O	0.06001	0.6109	0.93736	0.0663	0.61167	0.94417	0.16797

Table S3: Comparison of the positions of lanthanum cations obtained by DFT with those from diffraction in the disorder model $Fm\bar{3}m$. Last column prints the distance between both positions. W cations placed in La2/W2 positions used for DFT calculations are also included.

	x-DFT	y-DFT	z-DFT	x-diff.	y-diff.	z-diff.	Dist(Å)
La1 La	0.00058	0.00227	0.00038	0.00000	0.00000	0.00000	0.02753
La2 La	0.99037	0.51802	0.25143	0.00000	0.50000	0.25000	0.23059
La3 La	0.50916	0.00009	0.24895	0.50000	0.00000	0.25000	0.10504
La4 La	0.51199	0.51479	0.00614	0.50000	0.50000	0.00000	0.25322
La5 La	-0.00111	0.23275	0.13724	0.00000	0.23590	0.13205	0.12187
La6 La	0.01307	0.74254	0.11749	0.00000	0.73590	0.11795	0.16417
La7 La	-0.0012	0.26658	0.38207	0.00000	0.26410	0.38205	0.0308
La8 La	0.00095	0.77087	0.36959	0.00000	0.76410	0.36795	0.08475
La9 La	0.23422	0.00304	0.13572	0.23590	0.00000	0.13205	0.09076
La10 La	0.26334	0.00397	0.38259	0.26410	0.00000	0.38205	0.04676
La11 La	0.73604	0.01274	0.116	0.73590	0.00000	0.11795	0.14892
La12 La	0.76853	0.01275	0.36699	0.76410	0.00000	0.36795	0.15238
La13 La	0.23732	0.26922	0.49781	0.23590	0.26410	0.50000	0.07696
La14 La	0.74248	0.25063	0.99672	0.73590	0.23590	0.00000	0.19465
La15 La	0.24852	0.74799	0.99707	0.23590	0.73590	0.00000	0.20602
La16 La	0.76808	0.74448	0.50087	0.76410	0.73590	0.50000	0.10748
La17 La	0.27129	0.50036	0.36411	0.26410	0.50000	0.36795	0.11765
La18 La	0.24495	0.5035	0.11743	0.23590	0.50000	0.11795	0.10907
La19 La	0.7654	0.50285	0.38342	0.76410	0.50000	0.38205	0.04651
La20 La	0.75013	0.50501	0.12864	0.73590	0.50000	0.13205	0.18504
La21 La	0.23961	0.76566	0.25164	0.23590	0.76410	0.25000	0.05803
La22 La	0.7623	0.76861	0.24634	0.76410	0.76410	0.25000	0.09818
La23 La	0.73404	0.27152	0.2516	0.73590	0.26410	0.25000	0.09268
La24 La	0.50111	0.24382	0.38159	0.50000	0.23590	0.38205	0.08997
La25 La	0.50142	0.75466	0.37277	0.50000	0.76410	0.38205	0.23327
La26 La	0.50319	0.25275	0.11976	0.50000	0.23590	0.11795	0.1959
La27 La	0.50008	0.74181	0.13285	0.50000	0.73590	0.13205	0.06844
La28 La	0.0023	0.00693	0.49951	0.00000	0.00000	0.50000	0.08234
La29 La	0.98606	0.51826	0.74875	0.00000	0.50000	0.75000	0.25828
La30 La	0.50587	0.99484	0.74847	0.50000	0.00000	0.75000	0.09381
La31 La	0.50287	0.50505	0.4983	0.50000	0.50000	0.50000	0.07522
La32 La	0.00748	0.23731	0.63115	0.00000	0.23590	0.63205	0.08742
La33 La	0.00527	0.74354	0.61642	0.00000	0.73590	0.61795	0.10923
La34 La	0.00018	0.26163	0.88238	0.00000	0.26410	0.88205	0.02865
La35 La	0.00424	0.77326	0.86648	0.00000	0.76410	0.86795	0.1175
La36 La	0.23398	-0.00193	0.6324	0.23590	0.00000	0.63205	0.03142
La37 La	0.2637	0.00337	0.88228	0.26410	0.00000	0.88205	0.03828
La38 La	0.73841	0.01253	0.61779	0.73590	0.00000	0.61795	0.14287
La39 La	0.76484	0.00586	0.8683	0.76410	0.00000	0.86795	0.06648
La40 La	0.23818	0.23817	0.00657	0.26410	0.23590	0.00000	0.32579

La41 La	0.73461	0.23734	0.49827	0.73590	0.23590	0.50000	0.0443
La42 La	0.26645	0.77163	0.49872	0.26410	0.76410	0.50000	0.09269
La43 La	0.75186	0.75398	0.00365	0.73590	0.76410	0.00000	0.22643
La44 La	0.22545	0.51181	0.87492	0.23590	0.50000	0.88205	0.23763
La45 La	0.23988	0.51021	0.61078	0.23590	0.50000	0.61795	0.20171
La46 La	0.73616	0.49854	0.86961	0.73590	0.50000	0.86795	0.04064
La47 La	0.75506	0.50172	0.62148	0.76410	0.50000	0.61795	0.12963
La48 La	0.27322	0.72993	0.74574	0.26410	0.73590	0.75000	0.15463
La49 La	0.74129	0.75068	0.75064	0.73590	0.73590	0.75000	0.17641
La50 La	0.76011	0.25094	0.74911	0.76410	0.23590	0.75000	0.17505
La51 La	0.5085	0.23605	0.8715	0.50000	0.23590	0.88205	0.25425
La52 La	0.49412	0.73668	0.87043	0.50000	0.73590	0.86795	0.08642
La53 La	0.50314	0.27628	0.63232	0.50000	0.26410	0.63205	0.14071
La54 La	0.5009	0.77133	0.61418	0.50000	0.76410	0.61795	0.11719
W1 W	0.26339	0.25697	0.24974	0.26410	0.26410	0.25000	0.08029
W6 W	0.24892	0.24727	0.74329	0.23590	0.23590	0.75000	0.24459