Supplementary Materials

Local structure and Magnetic properties analysis of the $La_xEu_{1-x}PO_4$ solid-solutions

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Supplementary Figures

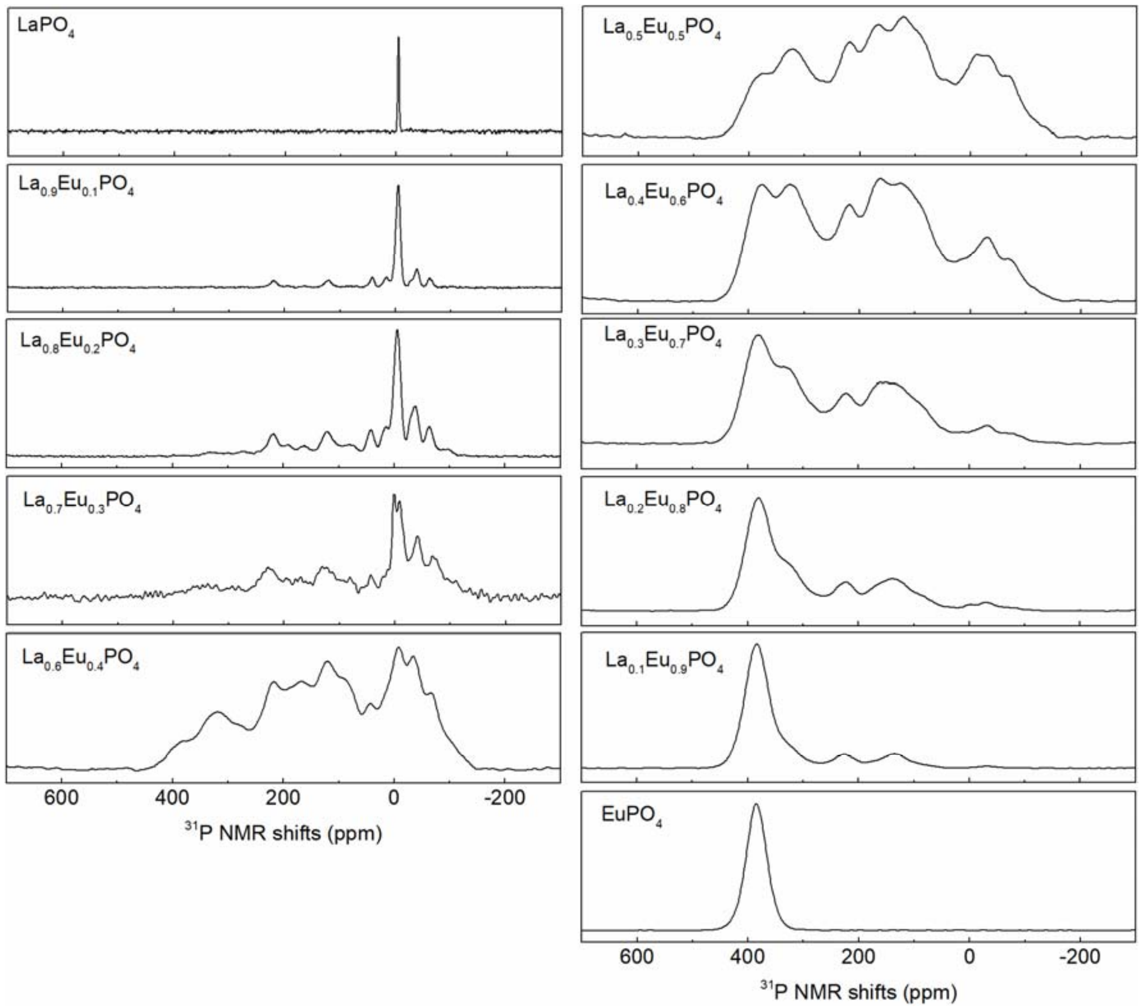

Figure S 1: ^{31}P MAS NMR spectra of the $La_xEu_{1-x}PO_4$ series acquired at a spinning rate of 60 kHz on a 4.7 T Bruker NMR spectrometer.

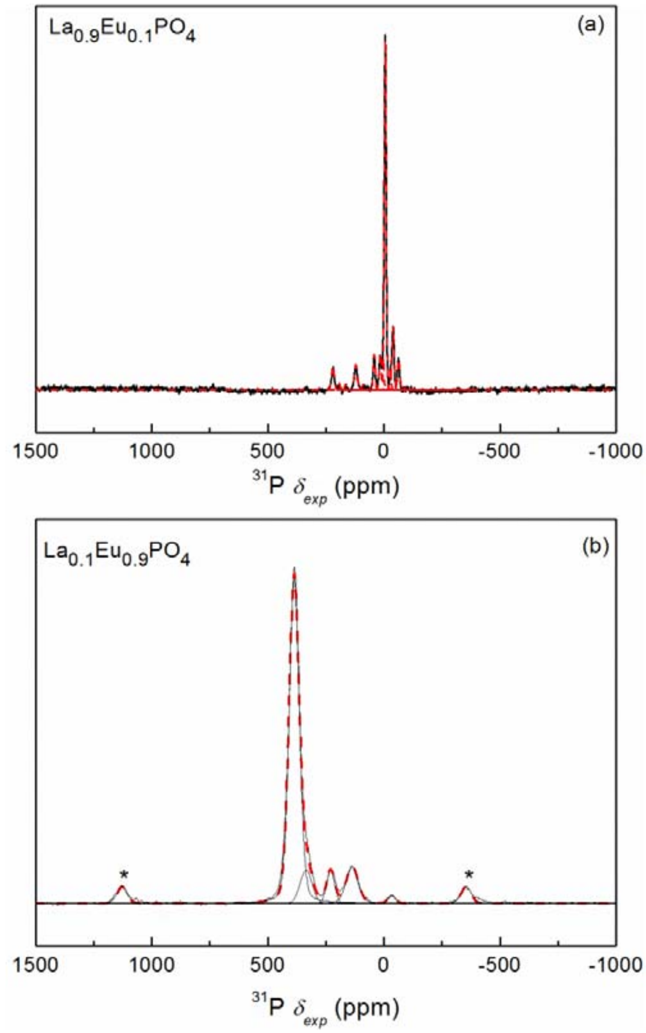

Figure S 2: Full ^{31}P MAS NMR spectra of the $La_xEu_{1-x}PO_4$ samples (x=0.9 and 0.1) acquired at a spinning rate of 60 kHz on a 4.7 T Bruker NMR spectrometer.

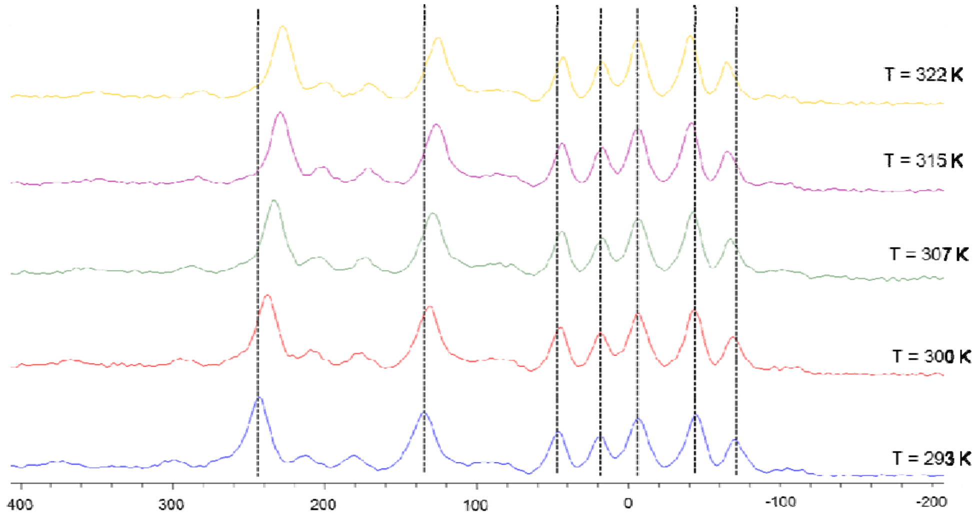

Figure S 3: ^{31}P MAS-NMR spectra acquired at different temperatures for $La_{0.9}Eu_{0.1}PO_4$. The dashed lines are guides for the eye.

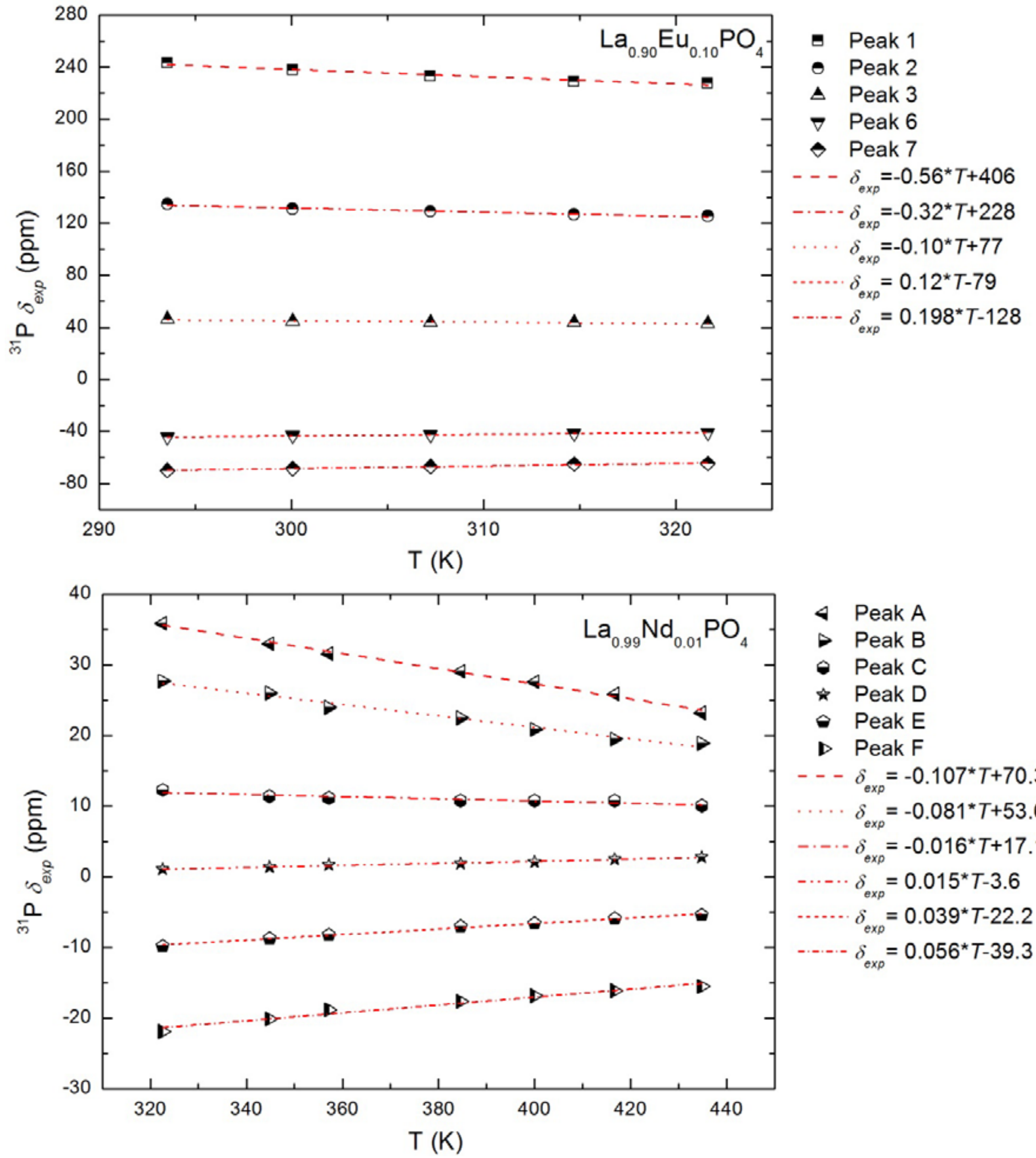

Figure S 4: Variation of the peaks position with temperature for the $La_{0.9}Eu_{0.1}PO_4$ and $La_{0.99}Nd_{0.01}PO_4$[1] solid solutions. In the present study, the experiments were recorded by at spinning frequencies of 45 kHz and varying the temperature between 293 and 322 K.

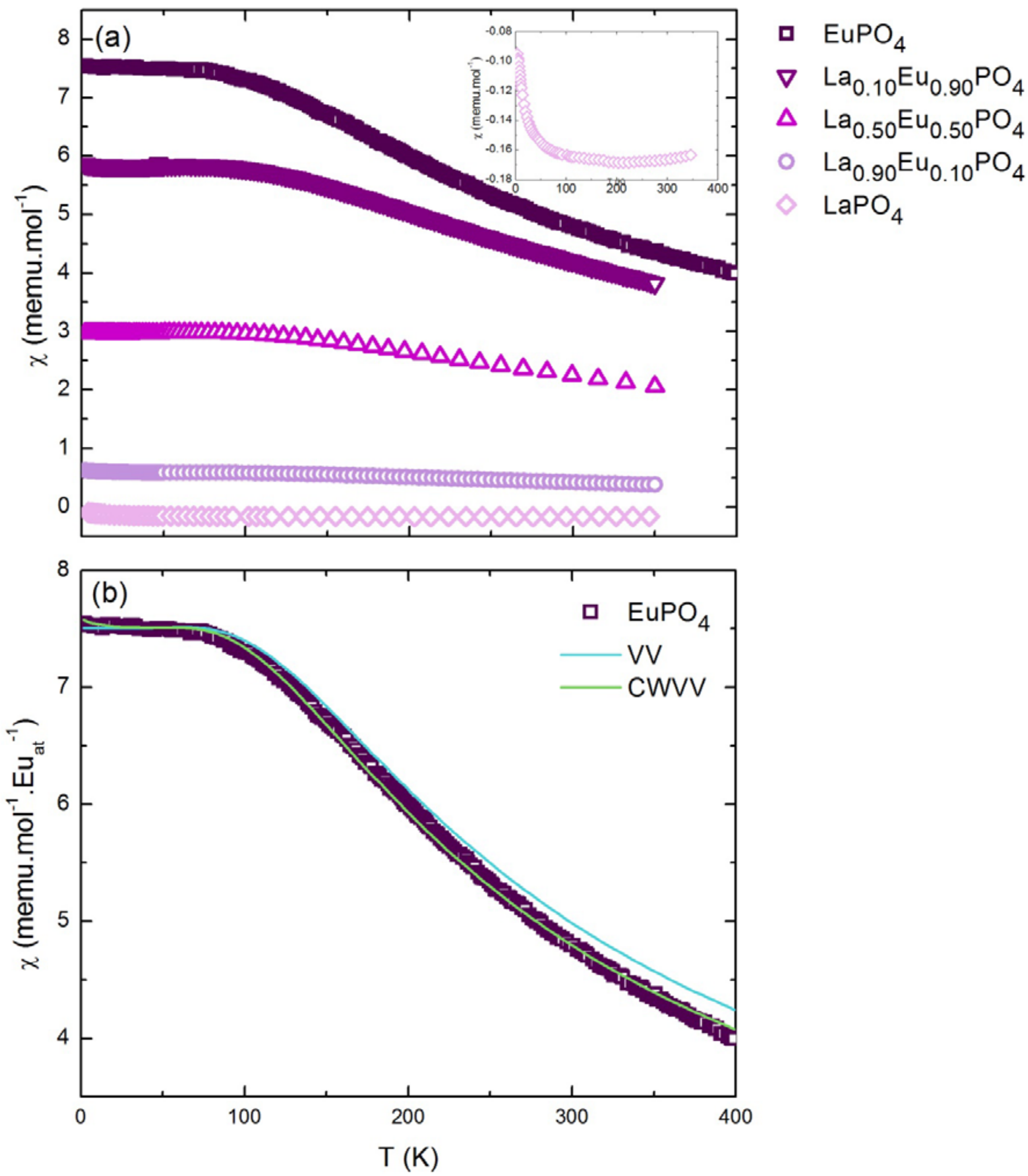

Figure S 5: Magnetic susceptibility curves and their corresponding fits. The inset shows a zoom on the $LaPO_4$ magnetic susceptibility.

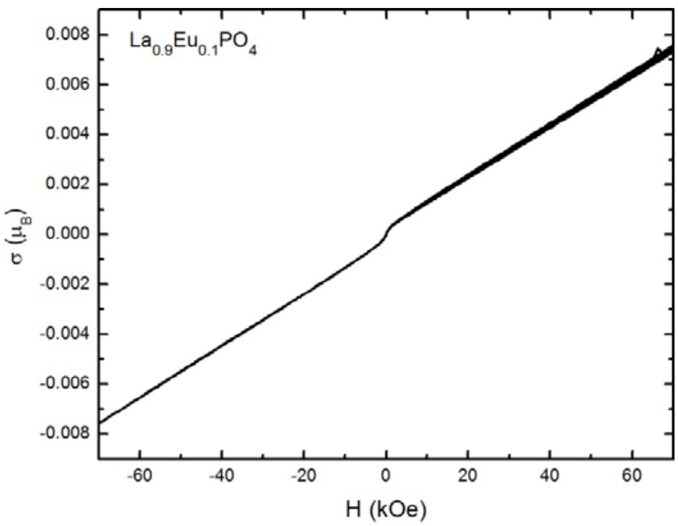

Figure S 6: Small hysteresis loop observed for $La_{0.9}Eu_{0.1}PO_4$.

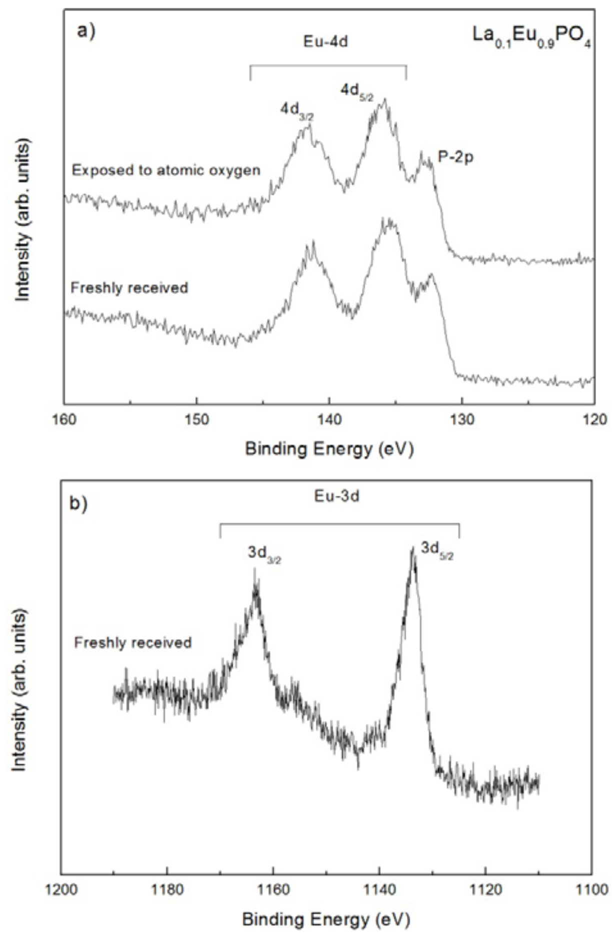

Figure S 7: XPS spectra of $La_{0.1}Eu_{0.9}PO_4$ in the energy range of a) the Eu-4d and P-2p orbitals and b) the Eu-3d orbital.

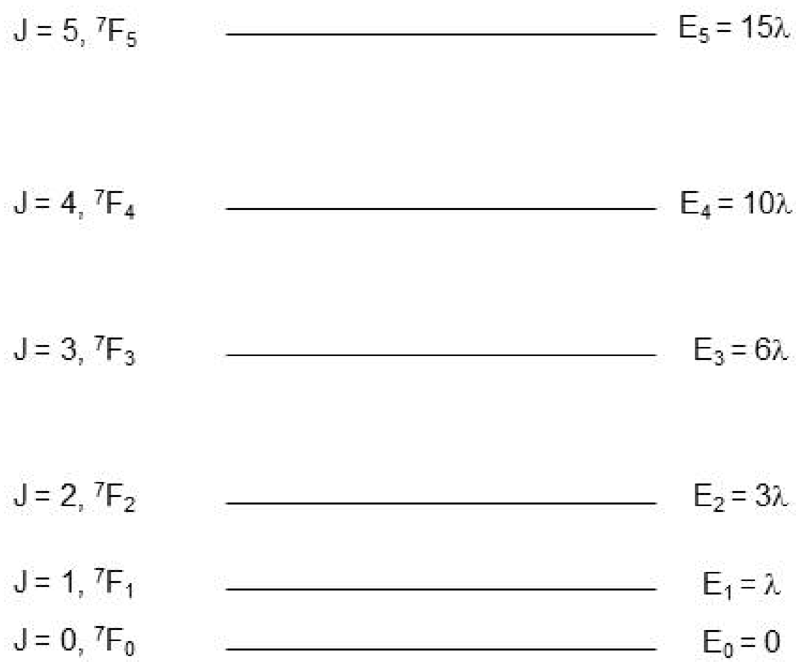

Figure S 8: Energy levels of the lowest multiplet ^7F_J of Eu^{3+} at $B_0 = 0$ T.

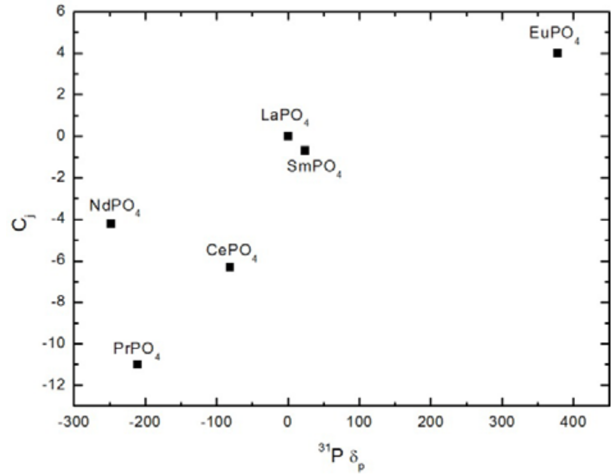

Figure S 9: Plot of the C_j constants[2] against the experimental shifts for the $LnPO_4$ series considering a constant A_{iso}.

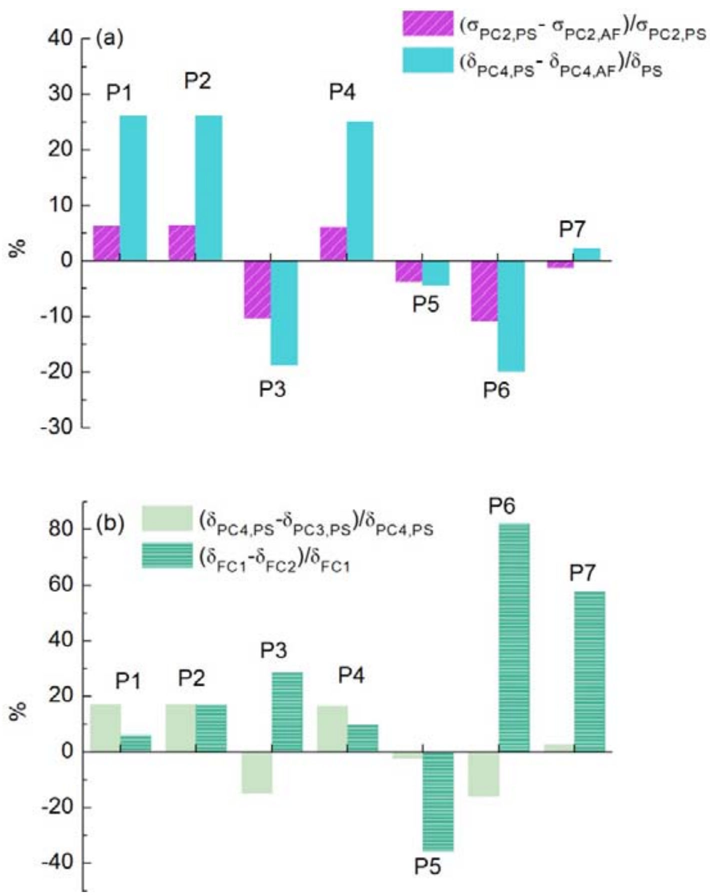

Figure S 10: Relative differences (in %) between (a) the shielding/shifts using the same approach but two sets of CFP and EL, and (b) the δ_{PC} calculated using the two approaches or the two clusters using the CFP and EL determined during this study.

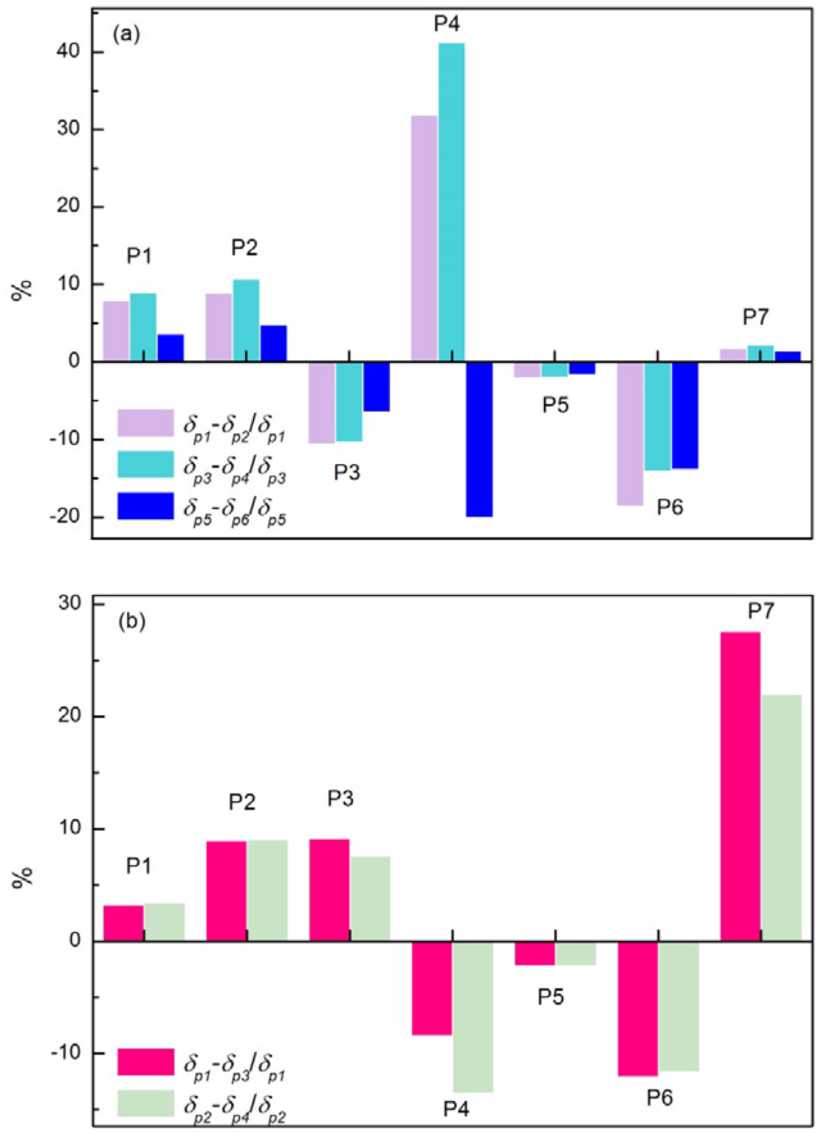

Figure S 11: Relative differences (in %) between the theoretical paramagnetic shifts.

Supplementary Tables

Table S1: P-Ln distances (r), P-O-Ln angle considering the crystalline structure (θ_c), polar angle (θ_s) and azimuthal angle (φ_s) considering the Eu or La atom at the origin.

	$LaPO_4$					$EuPO_4$			
	r(Å)	θ_c(°)	θ_s(°)	φ_s(°)	r_{APO}(Å)	r(Å)	θ_c(°)	θ_s(°)	φ_s(°)
P1	3.217	174.5	86.5	88.96	3.216	3.114	174.8	102.9	88.4
P2	3.293	0	96.6	84.4	3.295	3.241	0	80.7	84.6
P3	3.503	78.8	87.1	-17.2	3.505	3.458	77.4	80.1	-16.6
P4	3.768	98.7	132.5	-23.9	3.766	3.681	99.1	140.6	-8.5
P5	3.769	110.2	21.4	-46.6	3.768	3.640	110.3	36.3	-60.1
P6	3.782	69.4	78.3	17.1	3.782	3.656	69.6	77.5	13.3
P7	3.816	109.1	138.1	32.89	3.822	3.711	108.6	142.2	13.0

Table S 2: Relaxation times T_1 defined considering 3 main "regions" for the solid-solutions.

Sample name	Peak range	δ_{exp} (±0.2ppm)	FWHM (ppm) (± 5 %)	T_1 (s) (± 5 %)
$La_{0.8}Eu_{0.2}PO_4$				
	1	218.2	24.5	0.38
	2	120.6	27.7	0.61
	3	42.7	15.7	1.6
	4	15.0	19.6	2.5
	5	-6.4	15.1	9.2
	6	-38.2	16.9	3.1
	7	-63.6	18.4	2.5
$La_{0.7}Eu_{0.3}PO_4$				
	R1			--
	R2	249.9 to 72.7		0.58
	R3	72.7 to -155.1		2.95
$La_{0.6}Eu_{0.4}PO_4$				
	R1	501 to 253.5		0.28
	R2	253.5 to 58.3		0.53
	R3	58.3 to -223.8		1.8s
$La_{0.5}Eu_{0.5}PO_4$				
	R1	501 to 253.5		0.29
	R2	253.5 to 23.9		0.5
	R3	23.9 to -205.7		1.4
$La_{0.4}Eu_{0.6}PO_4$				
	R1	504.8-264.4		0.2
	R2	264 to 35		0.41
	R3	34.7 to -194.9		2.3
$La_{0.3}Eu_{0.7}PO_4$				
	R1	501 to 263		0.25
	R2	263 to 37		0.43
	R3			--
$La_{0.2}Eu_{0.8}PO_4$				
	1	386.4		0.21
	2	335		0.25
	3	229.5		0.31
	4	136.7		0.43
	5	-33.6		--

Table S 3: Relative peak intensities (%) at various x values in the $La_xEu_{1-x}PO_4$ series for each $(P(La)_y(Eu)_{7-x}$ unit (with $0 \leq y \leq 7$) calculated using the randomly distributed network (RDN) model.

Units	x								
	0.9	0.8	0.7	0.6	0.5	0.4	0.3	0.2	0.1
$P(La)_7(Eu)_0$	48	21	8.2	2.8	0.8	0.2			
$P(La)_6(Eu)_1$	37	36.7	24.7	13.1	5.5	1.7	0.4		
$P(La)_5(Eu)_2$	13	27.5	31.8	26.1	16.4	7.7	2.5	0.4	
$P(La)_4(Eu)_3$	2	11.5	22.7	29	27.3	19.3	9.7	2.9	
$P(La)_3(Eu)_4$		2.9	9.7	19.3	27.3	29	22.7	11.5	2
$P(La)_2(Eu)_5$		0.4	2.5	7.7	16.4	26.1	31.8	27.5	13
$P(La)_1(Eu)_6$			0.4	1.7	5.5	13.1	24.7	36.7	37
$P(La)_0(Eu)_7$				0.2	0.8	2.8	8.2	21	48

Table S 4: Twenty seven calculated B_q^k (cm^{-1}) parameters.

k	q	B_q^k
2	0	-623.214
2	1	-64.7431
2	-1	-42.1616
2	2	71.09481
2	-2	-13.2061
4	0	-321.383
4	1	470.4191
4	-1	190.8043
4	2	609.9013
4	-2	-49.677
4	3	511.5524
4	-3	-393.587
4	4	249.3432
4	-4	166.4712
6	0	606.2701
6	1	102.0181
6	-1	84.52455
6	2	-285.413
6	-2	41.23308
6	3	-369.142
6	-3	297.2502
6	4	36.26437
6	-4	53.23284
6	5	-274.948
6	-5	51.78076
6	6	-66.0227
6	-6	-196.456

Table S 5: Energy levels (cm^{-1}) measured experimentally (Exp) and calculated theoretically (Theo).

	$La_{0.9}Eu_{0.1}PO_4$	$LaPO_4$-doped 1-5%Eu^{3+} Luminescence		$EuPO_4$	Eu^{3+} free ion	
	Theo	Exp	Theo	Theo	Theo	Theo[3]
$^7F_0$						
	0	0	0	0	0	0
$^7F_1$						
	273.5	261	262	327	379	374
	438	406	411	382		
	462	464	458	404		
7F_2						
	931.3	943	954		1043	1036
	1023		978			
	1053	1021	1019			
	1143	1096	1091			
	1192	1178	1177			
$^7F_3$						
	1875	1853	1851		1896	1888
	1889	1881	1859			
	1948	1894	1895			
	1968	1917	1929			
	1992	1927	1936			
	2006	1944	1952			
	2012	1967	1962			
$^7F_4$						
	2744	2677	2675		2869	2866
	2806	2755	2751			
	2831	2792	2793			
	2880	2841	2852			
	2976	2863	2868			
	3015	2905	2906			
	3045	2933	2935			

3067	2963	2955		
3168		3006		

Cartesian coordinates of the cluster models

Model 1 ($P_1La_6Gd_1O_{25}H_{21}$)

P	-0.057703	0.220772	-0.035765
O	0.427236	-0.098999	1.403164
O	-0.848535	-1.051057	-0.493262
O	1.092124	0.459872	-1.054013
O	-0.881530	1.525844	-0.094097
Gd	-0.690676	-2.294643	1.996706
La	0.428885	2.860224	-1.806844
La	2.206565	0.415701	3.037988
La	-3.377507	-1.307575	-0.941519
La	3.581051	0.203296	-1.064937
La	-2.961187	2.450582	0.859538
La	0.682847	-2.507956	-2.106707
O	-2.013245	-2.822103	-2.191171
O	1.142454	5.065903	-2.107609
O	5.855974	0.517125	-1.465584
O	3.307215	-1.022283	1.115073
O	-2.442380	2.166283	3.056582
O	-0.796759	2.082549	-3.581413
O	0.786452	-1.600236	3.721362
O	-5.397721	-2.386124	-0.974188
O	2.770212	2.186319	-2.319360
O	-4.955265	3.639091	0.820365
O	-1.577511	4.000626	-0.420962
O	0.721674	-3.351720	0.371844
O	3.442874	0.192275	5.036099
O	0.435505	-1.191589	-4.005133
O	3.290159	1.654468	1.046624
O	0.905241	2.178992	3.774844
O	0.853353	-4.732599	-2.771088
O	-1.598713	-4.132285	3.004019
O	3.085357	-1.987871	-2.064766
O	-3.730966	1.028964	-1.170909
O	-2.969500	-1.356922	1.433593
H	-0.681467	1.151517	-3.830932
H	0.950253	5.794046	-1.505927
H	-1.859144	4.890896	-0.661068
H	3.257427	2.614896	0.954500
H	3.364272	2.896653	-2.588195
H	6.487308	0.920156	-0.858991
H	-1.618599	1.880544	3.476974
H	-5.461433	3.762579	0.008520
H	-3.670260	-1.453398	2.089166
H	-2.277884	-3.430418	-2.890347
H	-5.754535	-3.257603	-0.778957
H	-3.270399	1.502233	-1.883428
H	0.374992	-5.402792	-2.267458
H	3.721419	-2.710079	-2.014467

H	0.998826	-0.446233	-4.244579
H	2.897744	-1.892197	1.003640
H	0.313087	2.798205	3.333996
H	3.111622	0.738947	5.760863
H	1.007532	-1.986567	4.574658
H	1.203565	-4.172022	0.524790
H	-2.047105	-4.945979	3.242783

Model 2 ($Gd_1P_7La_{11}O_{40}H_{11}$)

Gd	0.22032000	0.19678300	-0.01391900
P	-2.95716200	-0.29062000	0.07266700
P	3.48175900	0.51484400	-0.36118600
P	-0.57664500	-1.93742300	2.98431300
P	-1.52196000	2.88531000	-2.09903200
P	1.84873700	-3.19960600	-0.35384100
P	0.73147300	3.43365700	1.22994600
P	-0.53179500	-1.55208800	-3.26548800
O	-2.13946200	0.92431100	0.56337100
O	-1.88103400	-1.25735300	-0.49726000
O	-3.82563000	-0.90526900	1.20132900
O	-3.96193600	0.04424700	-1.08130800
O	2.61306300	-0.10025000	0.76758600
O	2.47681800	0.84937200	-1.51485700
O	4.55757900	-0.45223800	-0.93111300
O	4.29930300	1.72919100	0.13041800
O	0.10931400	-0.64593700	2.42397300
O	0.59006500	-2.84342300	3.45860200
O	-1.54732000	-1.50756300	4.12036100
O	-1.49204600	-2.65328700	1.96711200
O	-0.35531400	1.97920100	-1.62465000
O	-2.49295100	3.31486600	-0.96302100
O	-0.83615500	4.17666300	-2.65936700
O	-2.43746400	2.16939300	-3.11628700
O	0.77285200	-2.23230900	0.21608100
O	2.71736900	-2.58394100	-1.48234700
O	2.85346700	-3.53393100	0.80000500
O	1.03112800	-4.41364500	-0.84534300
O	0.04544400	2.14255800	1.79038600
O	1.70176100	3.00420000	0.09388100
O	-0.43540500	4.33993900	0.75555900
O	1.64671100	4.14985800	2.24701000
O	0.38366900	-0.83640600	-2.24847700
O	-1.69839900	-0.64630100	-3.74000100
O	0.43897400	-1.98212000	-4.40164200
O	-1.21743100	-2.84380100	-2.70531800
La	-3.74593300	-2.46653700	3.11440600
La	-4.69126600	2.35605400	-1.96891100
La	2.69286200	-1.66127700	2.68080300
La	1.74760800	3.16107400	-2.40263200

La	-0.06574600	1.29961500	4.22783000
La	-1.32887700	-3.68651400	-0.26771400
La	5.11008700	-2.88136400	-0.70126800
La	-2.53808000	3.15789600	1.53358500
La	-3.80110200	-1.82821900	-2.96198800
La	3.90062900	3.96300200	1.09978600
La	2.63762600	-1.02327700	-3.39586000
O	5.58559500	4.84501300	2.22559700
H	6.35360800	5.22106200	2.66229200
O	3.50590200	4.59724300	-1.26563400
H	4.14192300	5.13550700	-1.75532300
O	4.93703600	-2.02848300	1.95812500
H	5.73882300	-1.55038100	2.20894000
O	2.14556500	0.41855000	4.38845200
H	2.92878100	0.76781800	4.83486200
O	-2.05168900	2.57450700	4.00904200
H	-2.80722000	2.58954400	4.61303900
O	-5.27289200	-1.90810900	4.68705000
H	-6.08346300	-2.01108700	5.19235700
O	-4.14347500	-4.27561900	1.87874500
H	-3.56789600	-4.96988200	1.48593300
O	-4.72528300	3.00044300	0.66180800
H	-5.55136300	2.75885100	1.10101500
O	-6.40571800	3.55864400	-2.69900900
H	-7.14878800	4.01037800	-3.10445300
O	2.34600700	1.49869500	-4.12636400
H	1.89913100	1.58219400	-4.98228800
O	4.74715800	-2.32197700	-3.18328400
H	5.48728600	-2.42855400	-3.79321700
O	7.09631400	-3.85034700	-0.84864600
H	7.90547300	-4.32072100	-1.06239000
O	-2.12953700	-5.67760900	0.52069000
H	-2.04556300	-6.63300300	0.57479600
O	-5.25349400	0.11806500	-3.37316700
H	-5.74027200	0.32073400	-4.18345600
O	-3.81810900	-3.44109700	-1.32845400
H	-4.34262800	-3.70761700	-0.55455300

References

1 A. C. Palke, J. F. Stebbins, *Am. Miner.*, **96**, 1343–1353 (2011).
2 R.M. Golding and P. Pyykkö, Mol. Phys., 26, 1389−1396 (1973).
3 G. S. Ofelt, *J. Chem. Phys.*, **38**, 2171 (1963).