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SUPPLEMENTARY MATERIAL

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Note: Table 1 here is also included in the main paper.

S1. Crystal-Field simulation details

Crystal-field calculations have been performed by applying the effective operator model describing the configuration of a rare earth ion in a crystalline surrounding. Eigenvectors and eigenvalues of the crystal-field levels were obtained by diagonalization of the combined free-ion and crystal-field energy matrices. The atomic quantum theory parametrizes the radial parts of the interactions, whereas the group theory completely solves their angular parts. The complete Hamiltonian is formed by two types of contributions. The atomic (freen ion) part, H_{FI} , including the several interactions needed to describe the ground configuration f^n of the rare earth ion is written as [1,2]:

$$H_{FI} = E_{AVE} + \sum_{k=2,4,6} F^{(k)} \cdot \dot{f}_{k} + \zeta_{4f} \cdot \sum_{i=1}^{N} \dot{s}_{i} \cdot \dot{l}_{i} + \alpha \cdot \dot{L}^{2} + \beta \cdot \ddot{G}(G_{2}) + \gamma \cdot \ddot{G}(R_{2})$$

+
$$\sum_{r=2,3,4,6,7,8} T^{(r)} \cdot t_{r} + \sum_{j=0,2,4} M^{(j)} \cdot m_{j} + \sum_{k=2,4,6} P^{(k)} \cdot p_{k}$$
(1)

where E_{AVE} is the spherically symmetric one-electron part of the Hamiltonian, $F^k(4f,4f)$ are the Slater integrals describing the electrostatic repulsion and ζ_{4f} parametrizes the spin-orbit interaction. The α , β , and γ parameters are associated with the two-body (Trees) correction terms, the three-particle configuration interaction is expressed by T^i . The electrostatically correlated spin-orbit perturbation is represented by the P^k parameters and those of spin-other-orbit relativistic corrections by the M^j parameters[3]. The spin-spin interaction, which also depends on the M^j parameters, having a rather minor contribution has not been included in the present calculation.

The crystal field acting on the rare-earth when embedded in a solid is described by the H_{CF} term of the Hamiltonian that represents the even part of the one electron crystal-field interactions defined as:

$$H_{FI} = \sum_{k=2,4,6} B_0^k \cdot C_0^{(k)} + \sum_{q>0}^{\leq k} \left[B_q^k \cdot \left(C_{-q}^{(k)} + (-1)^q C_q^{(k)} \right) + i B_q'^k \cdot \left(C_{-q}^{(k)} - (-1)^q C_q^{(k)} \right) \right]$$
(2)

where B_q^k and $B_q^{\prime k}$ are the real and imaginary crystal-field parameters which values are depending on the choice of the coordinate system used in the calculation.

Despite the increasing speed and power of modern computational techniques, the direct calculation of free ion parameters using ab initio methods is not yet an affordable line of work. Most of DFT computer packages operate with individual electron wave functions that make necessary an outsize, very tedious (and often sterile) computational effort to properly handle the crystal field effects in multi-electron configurations. Recent calculations [4] shows promising results but still suffering high inaccuracy. On the other hand, Hartree-Fock (*ab initio*) calculations of Slater $F^{(k)}$ and spin-orbit parameters ζ_{4f} that provide starting values for this calculations are not accurate enough for rare earth ions. Recent calculations [5-7] gives strongly overestimated values for Nd³⁺ ions preventing the use of direct ab initio methods to obtain the free ion parameters for our simulation. The calculations of the rest of the free ion parameters is too complex to be tried. Thus, to get a realistic approximation of the energy scheme of the Nd³⁺ ion in our system, a semiempirical approach has been performed in the second part of the main text, in which properly scaled Slater and spin-orbit parameters are used. The structural information obtained from previous DFT calculation [8], together with the crystal field model, allowed us to perform calculations that will help to make an interpretation of the luminescence experiments.

To reproduce the crystal field interaction, the SOM model [9] has been implemented due to its simplicity and because it uses only the nearest coordination environment of the Nd³⁺ ion. In the simulation, a slightly modified version of this model is used [10] which assumes that the effective charge has an exponential dependence with the bond length and verifies, in some way, the Pauling's second rule (the electrostatic valence rule). In this model the CF parameters are given by

$$B_{q}^{k} = \rho \left(\frac{2}{1 \pm \rho}\right)^{k+1} \langle r^{r} \rangle \sum_{L=1}^{N} \frac{g_{L} e^{2}}{R^{k+1}_{L}} \sqrt{\frac{4\pi}{2k+1}} (-1)^{q} Y_{k}^{-q} (\theta_{L}, \varphi_{L})$$
(3)

where ρ is the overlap between the metal and the ligand orbitals and the \pm sign characterizes the displacement of the charge barycenter from the middle metal-ligand distance, The minus sign indicates a metal-ligand covalent bond. In this expression the $\langle r^k \rangle$ are the radial expectation values (Freeman values), and the lattice sum extended

only to the first coordination sphere around the optically active ion. In the modified version the overlap ρ value is constant and the effective charge of the ligands, $g_L = g_0 e^{(A-R_L)/0.37}$, follows an exponential law with the ligand distance, as usual in bond valence model, in which *A* is a parameter that represent the nominal length of a bond of unit valence.

For the Nd³⁺-doped monoclinic monazite LaVO₄ samples, we assume that a small quantity of La³⁺ ions, lying on a C_I non-symmetry site, are substituted by Nd³⁺ ions without relevant structural distortions due to the similarity of their ionic radius. In this low symmetry, the degeneracies of the ^{2S+1}L_J multiplets, are completely lifted giving rise to 182 Kramers-degenerate Stark levels. In this low symmetry, the selection of quantization axis is arbitrary. Thus, there are 27 different real B_q^k and imaginary $B_q'^k$ crystal-field (CF) parameters and, since parameters values depends on the selection of the reference system, an arbitrary axis selection leads to a completely different set of CF parameters giving the same energy level positions. This fact makes difficult to understand the CF parameters meaning and follow they pressure variation. This situation can be even worse at high pressures, after the phase transition occurs, when the Nd³⁺ ions will occupy two different sites both with C_I local-symmetry. Therefore, in order to simplify the description of the crystal-field interaction, we analysed the crystal field simulation results using the rotationally invariant crystal-field strength parameter[11-13]:

$$S = \left[\sum_{k=2,4,6} (S^{(k)})^2\right]^{1/2} = \left[\frac{1}{3}\sum_{k=2,4,6} \frac{1}{2k+1} \left(\left(B_0^k\right)^2 + 2\sum_{\substack{q \le k \\ q > 0}} \left(\left(B_q^k\right)^2 + \left(B_q^{\prime k}\right)^2 \right) \right) \right]^{1/2}$$
(4)

which value, independent on the axis selection, estimates the overall crystal field felt by the central ion. Moreover, it is possible to separate the rank-*k* contribution to the *S* parameter. Because the dependence of CF parameters with the distance follows a $\sim 1/R^{(k+1)}$ dependence (being R the distance between the Nd³⁺ ion and its nearest oxygen ligands) a roughly, but simple, correlation of the crystal-field interaction with the ligand distance can be done by means the $S^{(k)}$ values. Indeed, is it possible to estimate the importance of the different contibutions as a percentage [14]:

$$\% S^{(k)} = 100 \left(\frac{S_{(k)}}{S}\right)^2$$

that characterizes the influence of the ligands charge at short (k=6), medium (k=4), and long (k=2) average metal-ligand distances.

S2.- Additional information about simulation results

The simulation procedure starts obtaining a set of Free-Ion parameters that, together with the calculated CF parameters using the modified SOM model on the structural data for ambient pressure lattice, allow us to achieve, as accurate as possible, an approximation to the ambient pressure experimental energy levels. The approximation reported by Antic-Fidancev *et al.* [15], is used for comparison purposes. The CF parameters obtained in our approach to the same experimental energy levels using the true C_1 symmetry, and the Free-Ion Hamiltonian parameters used in this calculation are reported in Table 1.

Once we have obtained a set of free ion parameters allowing an adequate description of the system at ambient pressure, the modified SOM model has been used, taking into account the available crystallographic data of the LaO₉ (Site I) environment in the LPphase and the LaO₉ (Site I*) and LaO₁₀ (Site II) environments in the HP-phase to obtain sets of CF parameters for each site at every pressure. The values; $\rho = 0.065$ and $g_0 = 2.0$ have been used for the overlap and charge factors for modified SOM model in this calculation. A covalent character was used for Nd-O bond. Concerning to the free-ion parameters, a linear reduction of the Slater integrals (-21.9 cm⁻¹/GPa) and a coupled decrease of the spin-orbit parameter (-0.269 cm⁻¹/GPa) have been assumed from their ambient pressure values. All other free-ion parameters were held fixed. Selected parameter sets near the phase transition are included in Table I.

Energy levels obtained at ambient pressure are given in Table S2. Because of the CF parameter values are strongly dependent on the axis selection, in the figures S1 and S2 we report a plot of the environment and the axis selection used in the calculation of the CF parameters reported in Table 1. Additional structural data are included in Table S3.

(5)

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Atomic ^(a)	C _{2v} symmetry	LP Phase Simulation		HP Phase Simulation		
and		Site I		(12.9 GPa)		
crystal-	Ambient	Ambient	(11.2 GPa)	Site I*	Site II	
field	pressure	pressure				
parameters						
$F^{(2)}$		71663.88	71418.6	71380.7	71380.7	
$F^{(4)}$		51963.19	51785.6	51758.1	51758.1	
F ⁽⁶⁾		35303.00	35180.8	35162.1	35162.1	
ζ_{4f}		881.02	878.01	877.54	877.54	
0						
B_0^2	-830	23.6	83.6	-300.5	178.8	
B_1^2	0	322.8	545.0	-634.4	-32.7	
B'_{1}^{2}	0	90.2	363.9	-66.3	-182.2	
B_{2}^{2}	213	-400.7	-487.7	-117.0	144.6	
B'_2^2	0	-423.4	-531.6	-360.1	-202.4	
B_0^4	-769	379.7	741.3	745.5	254.0	
B_1^4	0	-22.0	38.1	182.0	548.0	
B'_{1}^{4}	0	242.8	241.6	-82.0	-14.8	
B_{2}^{4}	562	-202.0	-112.2	95.5	-79.6	
B'_2^4	0	244.1	342.9	-39.2	179.0	
B_{3}^{4}	0	-59.3	-34.6	334.2	-32.3	
B'_{3}^{4}	0	-43.2	-66.9	-43.1	128.0	
B_4^4	383	553.3	558.2	165.9	227.4	
B'_4^4	0	-312.4	-337.6	-71.1	-272.5	
B_{0}^{6}	-798	319.4	560.6	40.4	683.4	
B_{1}^{6}	0	97.6	257.3	-494.7	864.0	
B'_{1}^{6}	0	511.1	763.7	-526.1	235.7	
B_{2}^{6}	-702	-364.0	-368.9	531.8	718.9	
B'_2^6	0	-6.3	38.6	-151.2	-148.9	
B_{3}^{6}	0	-115.2	-138.2	33.4	183.0	
B'_{3}^{6}	0	22.9	61.0	-249.3	95.1	
B_{4}^{6}	-105	379.6	283.7	353.0	-41.0	

Table 1. Free Ion CF parameters and crystal field strength values at ambient pressure, and at pressures near the phase transition, obtained using lattice positions from *ab initio* calculations. CF parameters reported at ambient pressure in approximated C_{2v} symmetry (from ref. [15]) are also included.

B'_4^6	0	-17.6	-181.7	-19.8	-185.2
B_{5}^{6}	0	241.2	302.0	-717.1	-168.1
$B_{5}^{\prime 6}$	0	-285.8	-236.0	154.3	715.6
B_{6}^{6}	-563	-577.4	-696.0	821.1	-16.0
$B_{6}^{\prime 6}$	0	-159.6	-320.5	359.6	-541.5
S	408,1	405.9	535.3	485.2	425.0
S ⁽²⁾	228	245.6	356.5	281.7	122.3
$S^{(4)}$	237	217.9	257.6	187.5	195.2
S ⁽⁶⁾	241,7	238.7	305.0	347.7	357.1
%S ⁽²⁾	24	37	44	34	8
%S ⁽⁴⁾	32	29	23	15	21
%S ⁽⁶⁾	44	35	32	51	71

^(a) Fixed atomic parameter (in cm⁻¹) from ref. [16]: $\alpha = 22.08$; $\beta = -650$; $\gamma = 1586$; $T^2 = 377$; $T^3 = 40$; $T^4 = 63$; $T^6 = -292$; $T^7 = 358$; $T^8 = 354$; $M^0 = 1.97$; $M^2 = 0.56 M^0$; $M^4 = 0.38 M^0$; $P^2 = 255$; $P^4 = 0.75 P^2$; $P^6 = 0.5 P^2$

 Energies (cm ⁻¹)				Energies (cm ⁻¹)		
Experimental	Calculated Ref [15]	Calculated This work	Exp	perimental	Calculated Ref [15]	Calculated This work
 0	3.2	0		11404	11404	11410.4
67	81.2	86.1		11545	11538.4	11554.2
202	196.1	215.5		12430	12419.4	12431.6
323	339.5	347.9		12525	12505.2	12512.7
436	430.9	450.4		12595	12544.1	12540.2
1979	1977.3	1985.3		12595	12555.1	12575.1
2012	2034.3	2034.4		12667	12578.1	12586.9
2043	2042.5	2056		12752	12666.5	12670
2140	2131	2151.9		12788	12749.4	12760.9
2168	2180.7	2200			12795.7	12798.3
2222	2216.4	2226.9		13347	13354.7	13355.6
	3919.5	3937.1		13481	13459.1	13482.7
	3988.8	3990.7		13515	13522.4	13531
	4022.3	4018.3		13579	13566.3	13581.4
	4068.1	4114.5		13579	13580.8	13596.5
	4151.3	4177.4		13635	13625.3	13644.7
	4212.7	4204.1		14670	14661.8	14666.8
	4219.7	4244.3		14716	14709.9	14727.6
	5841.3	5843.1		14776	14750.7	14779.9
	5944.2	5938.4		14835	14820.2	14829.9
	6029.4	6009.3		14905	14897	14903.4
	6069.3	6173.5		15924	15940.3	15938
	6142.4	6230.4		15924	15945.9	15972.1
	6321.6	6317.4		15961	15967	15978.4
	6403.5	6388.6		15989	15986.9	15992.2
	6469.6	6454.8		16020	16003.9	16013.9

Table S2. Energy levels reported (from ref [15]) and calculated at ambient pressure with the parameters in Table 1

En	ergies (cm ⁻¹))	En	ergies (cm ⁻¹)
Experimental	Calculated Ref [15]	Calculated This work	Experimental	Calculated Ref [15]	Calculated This work
16052	16035.6	16039.1	20942	20916.4	20934.1
17000	17060.3	17045.6	20996	21002.6	21002.5
17152	17113.8	17153.9	21018	21039.2	21044.9
17221	17225.1	17226.2	21039	21065.3	21071.3
17290	17281.9	17301.2	21076	21100.3	21102.6
17329	17299.3	17336.8	21139	21133.9	21168.3
17368	17353.2	17361.3	21209	21188.9	21203.9
17415	17421.2	17402.3	21323	21318.7	21351.4
18947	18929.3	18947.5	21363	21378	21396.9
18979	18997.3	19002.4	21445	21450.4	21450.9
19043	19095	19088.2		21471.3	21462.9
19145	19132.2	19163.7	21498	21496.1	21506
19351	19344.8	19350.4		21515.1	21535.3
19403	19402.7	19423.3		21549	21577.2
	19435.6	19465.3	21566	21589.3	21628.3
	19472.8	19489.6	21629	21648	21645.4
19498	19496.6	19509.7	21668	21663.8	21660
	19524.3	19534.7	21698	21715.2	21694
	19546.5	19556.2	21744	21744.4	21770.7
	19602.9	19573.4	21861	21869.1	21886.1
19618	19627.6	19632.4	22012	22033	22039.6
19700	19667.2	19707.3	23229	23220.5	23229.8
19800	19858.9	19830.2		23654	23657.3
20012	20015.4	20044.1		23845.5	23848.3

Site I						Site I	
Ambient pressure					P =	11.2 GPa	
R (Å)	θ (degrees)	φ (degrees)	q (e)	R (Å)	θ (degrees)	φ(degrees)	q (e)
2.473	21.79	104.18	0.830	2.386	19.16	11.32	0.869
2.480	93.64	86.83	0.816	2.392	90.18	83.22	0.854
2.492	49.51	269.24	0.789	2.424	115.00	13.65	0.784
2.497	15.92	12.16	0.779	2.427	96.86	208.16	0.777
2.501	95.06	207.63	0.769	2.459	115.19	281.21	0.713
2.539	16.11	278.92	0.694	2.473	51.82	70.97	0.687
2.637	58.14	350.54	0.533	2.534	176.23	30.41	0.582
2.648	79.76	249.16	0.517	2.672	57.08	51.76	0.401
2.883	75.13	150.46	0.274	2.739	74.13	49.68	0.334
	Site	e I*			Sit	e II	
	P = 12	.9 GPa		P = 12.9 GPa			
R (Å)	θ (degrees)	$\phi(degrees)$	q (e)	R (Å)	θ (degrees)	φ(degrees)	q (e)
2.370	164.96	273.97	0.806	2.370	88.97	344.99	0.816
2.382	108.43	181.97	0.781	2.382	161.47	354.10	0.781
2.415	38.29	158.38	0.715	2.415	125.17	163.78	0.715
2.417	71.04	232.54	0.709	2.417	125.11	246.59	0.709
2.481	65.38	62.20	0.598	2.481	64.91	117.39	0.598
2.532	76.60	354.14	0.521	2.532	14.61	203.19	0.521
2.534	101.19	289.06	0.518	2.534	71.32	281.82	0.518
2.553	97.70	117.43	0.491	2.553	117.16	81.33	0.491
2.564	35.20	302.68	0.478	2.564	71.87	210.70	0.478
				2.644	61.37	43.22	0.384

Table S3. Spherical coordinates and effective charge of oxygen ligands in the several sites at selected pressures

Figure S1. The Site I at ambient pressure, showing the axis selection to obtain the results in Table I. The same axis selection was made for calculation at 11.2 GPa.



Figure S2. The Site I* (left) and Site II (right) in the HP phase (12.9 GPa), showing the axis selection to obtain the results in Table I.

