Electronic Supplementary Information

Theoretical investigation of the electronic structure and luminescence properties for $Nd_xY_{1-x}Al_3(BO_3)_4$ nonlinear laser crystal

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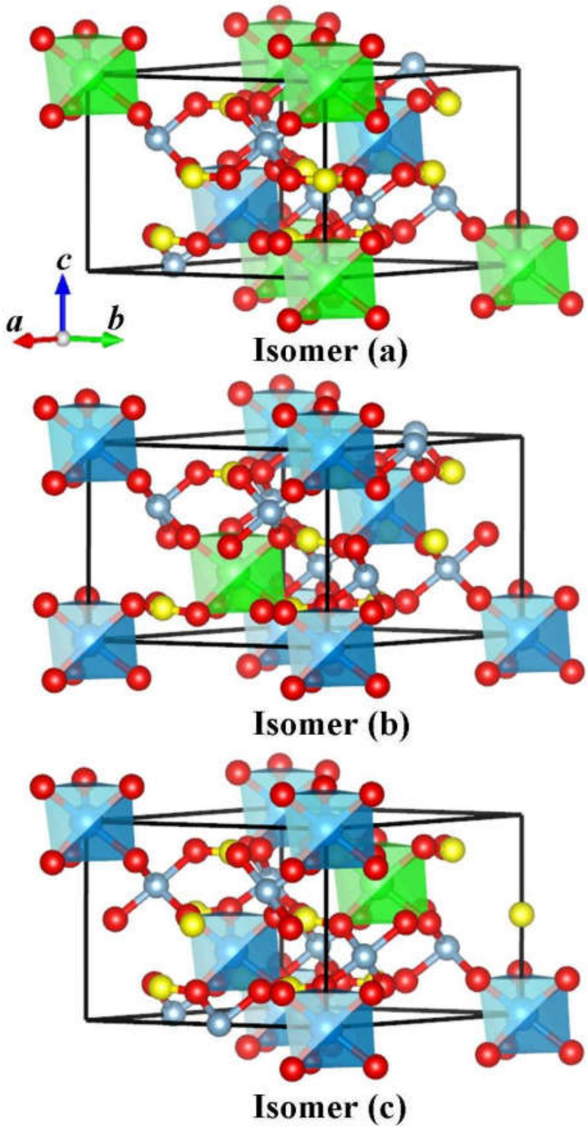

Figure S1. Coordination structures the optimized metastable (a), (b) and (c) for Nd:YAB. The yellow, red, gray, blue and green spheres represent B, O, Al, Y and Nd atoms, respectively.

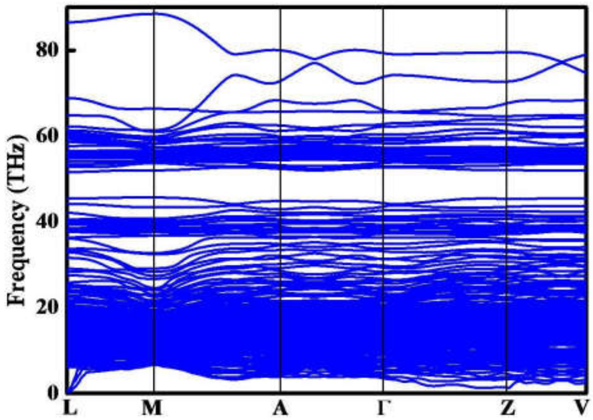

Figure S2. Phonon dispersion spectrum of the lowest energy structure for Nd-doped YAB.

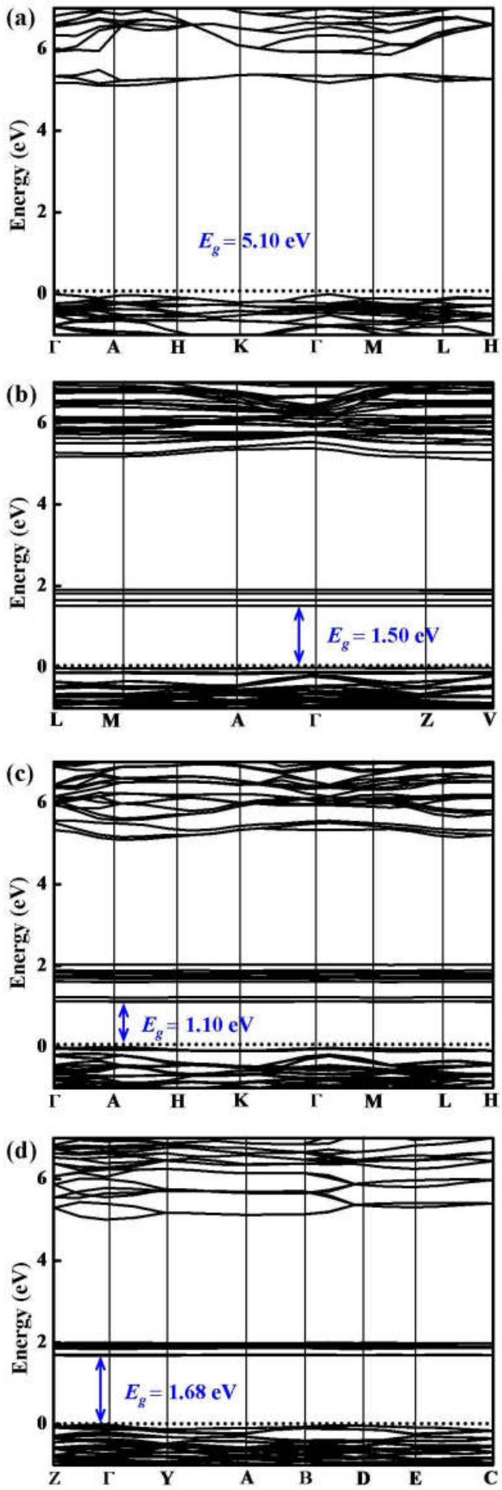

Figure S3. Calculated band structures of (a) YAB, (b) Nd:YAB, (c) γ-NAB and (d) β-NAB. The Fermi level is indicated by the dotted line.

Table S1. Structural parameters *a*, *b* and *c*, unit-cell volume, relative energies for the optimized NAB and metastable Nd:YAB.

	Space group	*a* (Å)	*b* (Å)	*c* (Å)	*V* (Å^3)	Δ*E* (eV)
β-NAB	*C*2/*c*	7.3370	9.4396	11.2586	757.978	0
γ-NAB	*R*32	9.4177	9.4177	7.3934	567.890	0.174
Nd:YAB	*C*2	9.3977	9.3977	7.3679	563.694	0.328
Isomer (a)	*C*2	9.3809	9.3809	7.3344	558.844	0.688
Isomer (b)	*P*1	7.3345	9.3765	9.3815	558.885	0.694
Isomer (c)	*P*1	7.3353	9.3773	9.3822	559.002	0.696

Table S2. Calculated *g*-factors for the excited states of Nd^{3+} in YAB. Available theoretical results are listed for comparison.

		Other[a]		Fit 1		Fit 2		Fit 3	
$^{2S+1}L_J$ (Sta.)	Γ	$g_{//}$	$g_{\perp}$	$g_{//}$	$g_{\perp}$	$g_{//}$	$g_{\perp}$	$g_{//}$	$g_{\perp}$
$^4I_{9/2}$	4	1.332	3.552	−1.414	3.400	−1.377	3.304	−1.400	3.309
	5,6	5.428	0	2.934	0	3.561	0	−0.586	0
	4	−0.200	2.832	2.769	−3.233	2.753	−3.028	2.768	−3.037
	5,6	3.191	0	3.974	0	4.354	0	4.373	0
	4	1.047	3.247	0.895	4.972	0.875	4.827	0.880	4.837
$^4I_{11/2}$	4	−4.139	3.189	4.140	−5.360	2.702	−5.683	2.735	−5.676
	5,6	6.232	0	7.650	0	7.605	0	7.655	0
	4	−1.753	0.665	−3.558	4.927	−2.557	5.245	−2.622	5.212
	4	−3.260	3.311	−9.161	0.428	−8.655	0.508	−8.638	0.524
	5,6	5.338	0	3.036	0	2.806	0	2.000	0
	4	1.432	5.248	0.860	−8.107	0.842	−8.100	0.854	−8.105
$^4I_{13/2}$	4	2.145	6.246	4.769	7.337	4.593	7.104	4.727	7.058
	5,6	6.843	0	9.110	0	8.918	0	8.952	0
	4	0.852	4.739	−6.512	−5.290	−5.537	−6.017	−5.651	−5.962
	4	6.064	3.048	−1.400	3.506	−0.638	5.638	1.130	5.751
	4	−4.405	3.837	7.421	−5.439	4.448	−6.691	3.957	−6.807
	5,6	6.425	0	3.568	0	3.321	0	3.670	0
	4	0.885	7.018	1.142	10.756	1.214	10.736	1.200	10.747
$^4F_{3/2}$	4	0.397	0.795	0.244	−1.312	0.156	−1.345	0.177	−1.337
	5,6	1.192	0	1.379	0	0.643	0	0.393	0

[a] Ref. [1].

Table S3. The calculated Stark levels (all in cm^{-1}) of Nd^{3+} in YAB. Available experimental and theoretical results are listed for comparison.

$^{2S+1}L_J$	Level No.	$E_{expt}{}^a$	$E_{expt}{}^b$	Present work E_{calc}	ΔE	Other $E_{calc}{}^b$
$^4I_{9/2}$	1	0	0	–11	11	–7
	2	48	49	52	–3	56
	3	109	147	153	–6	154
	4	165	271	284	–13	298
	5	289	323	339	–16	348
$^4I_{11/2}$	6	1945	1934	1933	1	1928
	7	1968	1948	1948	0	1940
	8	1982	1964	1967	–3	1962
	9	2082	2083	2084	–1	2086
	10	2127	2104	2101	3	2103
	11	2165	2142	2142	0	2143
$^4I_{13/2}$	12	3900	3898	3887	10	3891
	13	3912	3908	3899	9	3881
	14	3952	3924	3919	5	3910
	15	3931	4044	4038	6	4037
	16	4068	4075	4063	12	4064
	17	4097	4097	4091	6	4091
	18	4114	4147	4139	8	4139
$^4I_{15/2}$	19	5827	5851	5840	11	5847
	20	5886	5857	5848	9	5840
	21	5973	5924	5944	–20	5940
	22	6024	6073	6089	–16	6092
	23	6130	6099	6097	2	6105
	24	6170	—	6165	—	6173
	25	6234	6220	6218	2	6224
	26	6309	6281	6283	–2	6286
$^4F_{3/2}$	27	11391	11364	11355	9	11353
	28	11440	11436	11420	16	11418
$^4F_{5/2}$	29	12336	12363	12346	17	12341
	30	12391	12432	12428	4	12426
	31	12449	12455	12469	–14	12467
$^2H_{(2)9/2}$	32	12473	12530	12520	10	12546
	33	12500	12576	12566	10	12572
	34	12556	12627	12624	3	12626
	35	12648	12694	12690	4	12690
	36	12703	—	12711	—	12717
$^4F_{7/2}$	37	13313	13337	13357	–20	13351

	38	13370	13364	13366	–2	13370
	39	13385	13417	13418	–1	13419
$^4S_{1/2}$, $^4S_{3/2}$	40	13428	13472	13475	–3	13464
$^4S_{3/2}$	41	13491	—	13483	—	13470
$^4F_{7/2}$	42	13500	13483	13493	–10	13494
$^4F_{9/2}$	43	14604	14580	14584	–4	14575
	44	14632	14611	14614	–3	14607
	45	14655	14638	14642	–4	14635
	46	14768	14749	14760	–11	14760
	47	14773	14826	14830	–4	14835
$^2H_{(2)11/2}$	48	—	15790	15818	–28	15816
	49	15809	15816	15846	–30	15845
	50	15844	15827	15840	–13	15840
	51	15952	15936	15953	–17	15949
	52	15992	15974	15961	13	15964
	53	16014	16000	15988	12	15996
$^4G_{5/2}$	54	16880	16862	16876	–14	16867
	55	17050	17034	17041	–7	17050
	56	17076	17063	17069	–6	17070
$^4G_{7/2}$	57	17135	17170	17183	–13	17185
$^2G_{7/2}$	58	17188	17249	17228	21	17231
	59	17259	17282	17256	26	17263
	60	17352	17338	17330	8	17342
$^4G_{7/2}$	61	18779	18809	18801	8	18791
	62	18831	18873	18865	8	18872
$^2G_{7/2}$	63	18887	18925	18928	–3	18932
$^4G_{7/2}$	64	18954	18990	18972	18	18990
$^2K_{13/2}$	65	19011	19249	19251	–2	19255
	66	19091	19283	19289	–6	19288
$^4G_{9/2}$	67	19267	19369	19372	–3	19369
	68	19312	19375	19380	–5	19375
	69	19387	19394	19414	–20	19414
	70	19398	19425	19428	–3	19423
	71	19436	19451	19440	11	19437
$^2K_{13/2}$	72	19469	—	19504	—	19494
	73	19488	19569	19580	–11	19575
	74	19607	19699	19698	1	19682
	75	19723	19788	19788	0	19778
	76	19762	19820	19816	4	19817
$^2G_{9/2}$	77	19786	20807	20785	22	20778
	78	20833	20829	20821	8	20806
	79	20848	20905	20894	11	20925
	80	20947	20920	20917	3	20904
	81	—	21003	21004	–1	21012
$^2D_{3/2}$	82	—	21075	21076	–1	21092

	83	20947	21122	21141	–19	21140
$^4G_{11/2}$	84	—	21171	21192	–21	21186
	85	21225	21213	21231	–18	21227
	86	21105	21306	21319	–13	21317
$^2K_{15/2}$	87	21133	21365	21350	15	21353
	88	21195	21383	21370	13	21360
	89	21235	21443	21447	–4	21439
$^4G_{11/2}$	90	21326	21498	21489	9	21499
$^2K_{15/2}$	91	21413	21533	21540	–7	21529
	92	21461	—	21585	—	21577
$^4G_{11/2}$	93	21522	21621	21607	14	21620
	94	21598	21675	21663	12	21673
$^2K_{15/2}$	95	21633	—	21741	—	21718
	96	21691	21796	21790	6	21772
	97	21809	21813	21812	1	21804
$^2P_{1/2}$	98	23153	23131	23115	16	23130
$^2D_{5/2}$	99	23666	23628	23601	27	23624
	100	23719	23697	23721	–24	23712
	101	23786	23786	23786	0	23789
$^2P_{3/2}$	102	27750	26006	25997	9	25984
	103	27820	26094	26083	11	26072
$^4D_{3/2}$	104	28019	27773	27769	4	27773
	105	28074	27805	27779	26	27780
$^4D_{5/2}$	106	—	—	27964	—	27969
	107	28270	28035	28016	19	28015
	108	28422	28249	28246	3	28255
$^4D_{1/2}$	109	29846	28411	28410	1	28400
$^2I_{11/2}$	110	—	28812	28818	–6	28833
	111	—	29008	29037	–29	29032
	112	—	29036	29036	0	29049
	113	—	—	29298	—	29286
	114	—	29317	29310	7	29315
	115	—	—	29355	—	29345
$^2L_{15/2}$	116	—	29787	29780	7	29767
	117	—	—	29887	—	29846
	118	—	29848	29854	–6	29860
$^4D_{7/2}$	119	—	—	29900	—	29896
$^2L_{15/2}$	120	—	29991	30019	–28	30025
	121	—	—	30105	—	30098
$^4D_{7/2}$	122	—	30119	30138	–19	30133
$^2L_{15/2}$	123	—	—	30173	—	30162
$^4D_{7/2}$	124	—	—	30197	—	30203
	125	—	30209	30221	–12	30222
$^2L_{15/2}$	126	—	—	30254	—	30241
$^2I_{13/2}$, $^2L_{15/2}$	127	—	30269	30272	–3	30281

$^2I_{13/2}$	128	—	30304	30312	–8	30306
	129	—	30389	30393	–4	30384
	130	—	30498	30491	7	30500
	131	—	30517	30485	32	30501
	132	—	30654	30666	–12	30655
	133	—	—	30677	—	30676
	134	—	30699	30712	–13	30702
$^2L_{17/2}$	135	—	—	31335	—	31294
	136	—	31302	31300	2	31298
	137	—	31376	31364	12	31380
	138	—	31523	31502	21	31522
	139	—	31606	31583	23	31592
	140	—	—	31629	—	31628
	141	—	—	31680	—	31675
	142	—	—	31738	—	31730
	143	—	31756	31771	–15	31758
$^2H_{9/2}$	144	—	32556	32566	–10	32579
	145	—	32609	32588	21	32590
	146	—	32651	32653	–2	32657
	147	—	—	32682	—	32684
	148	—	32695	32702	–7	32696
$^2D_{(2)3/2}$	149	—	33050	33076	–26	33054
	150	—	33095	33098	–3	33094
	151	—	33885	33908	–23	33911
	152	—	33934	33929	5	33931
$^2H_{(1)11/2}$	153	—	—	33935	—	33946
	154	—	33988	34009	–21	34005
	155	—	34041	34038	3	34030
	156	—	—	34079	—	34064
	157	—	—	34103	—	34092
$^2D_{(2)5/2}$	158	—	34175	34155	20	34154
$^2H_{(1)11/2}$	159	—	34215	34188	27	34171

[a]Ref. [2].

[b]Ref. [3].

Table S4. Calculated wavelengths (λ), ED (A_{ED}) and MD (A_{MD}) radiative decay rates, branching ratios (β) and radiative lifetimes (τ) for spontaneous emission transitions between J-multiplets in Nd:YAB. Available theoretical and experimental results are also listed for comparison.

Transition		λ (nm)		A_{ED} (s^{-1})		A_{MD} (s^{-1})	β		τ (μs)	
		Present	Other	Present	Other	Present	Present	Other	Present	Other
$^4I_{11/2}$	$^4I_{9/2}$	5391		7.8		1.4	1		106835	
$^4I_{13/2}$	$^4I_{9/2}$	2611		21.1		0	0.66		31256	
	$^4I_{11/2}$	5063		9.0		2.0	0.34			
$^4I_{15/2}$	$^4I_{9/2}$	1700		6.3		0	0.17		26837	
	$^4I_{11/2}$	2482		19.6		0	0.53			
	$^4I_{13/2}$	4870		10.0		1.5	0.30			
$^4F_{3/2}$	$^4I_{9/2}$	891	895[b]	1664.4	1637[a]	0	0.49	0.493[a]	298	302[a]
	$^4I_{11/2}$	1067	1064[b]	1441.3	1430[a]	0	0.43	0.431[a]		
	$^4I_{13/2}$	1352	1325[b]	235.1	235[a]	0	0.07	0.071[a]		
	$^4I_{15/2}$	1872	1835[c]	11.5	12[a]	0	0.003	0.005[a]		
$^4F_{5/2}$	$^4I_{9/2}$	816	802[b]	2627.1		0	0.63		241	
	$^4I_{11/2}$	961		642.5		0	0.16			
	$^4I_{13/2}$	1187		763.0		0	0.18			
	$^4I_{15/2}$	1570		109.1		0	0.03			
$^2H_{(2)9/2}$	$^4I_{9/2}$	802	802[b]	296.7		6.1	0.50		1653	
	$^4I_{11/2}$	942		40.1		3.7	0.07			

	$^4I_{13/2}$	1158		122.9	0	0.20	
	$^4I_{15/2}$	1519		135.2	0	0.23	
$^4F_{7/2}$	$^4I_{9/2}$	756	750[a]	1573.8	0	0.39	246
	$^4I_{11/2}$	879		1405.5	0	0.34	
	$^4I_{13/2}$	1064		608.6	0	0.15	
	$^4I_{15/2}$	1361		475.8	0	0.12	
$^4S_{3/2}$	$^4I_{9/2}$	751	750[a]	1541.5	0	0.43	280
	$^4I_{11/2}$	873		880.0	0	0.25	
	$^4I_{13/2}$	1054		769.0	0	0.22	
	$^4I_{15/2}$	1346		374.0	0	0.10	
$^4F_{9/2}$	$^4I_{9/2}$	689	679[b]	189.4	1.6	0.06	313
	$^4I_{11/2}$	790	795[a]	940.2	1.4	0.30	
	$^4I_{13/2}$	937		1158.3	0	0.36	
	$^4I_{15/2}$	1159		895.5	0	0.28	

[a]Ref. [2]

[b]Ref. [4]

[c]Ref. [5]

Appendix – Method and equations for the calculations of transition intensities

The ED (A_{ED}) radiative decay rates can be written as[6-7]

$$A_{ED(SLJ\rightarrow S'L'J')}=\frac{16\pi^3e^2}{3\varepsilon_0hc^3}\frac{\nu^3}{(2J+1)}\chi_{ED}\sum_{\lambda=2,4,6}\Omega_{(\lambda)}\left|\left\langle l^NSLJ\left\|U^{(\lambda)}\right\|l^NS'L'J'\right\rangle\right|^2 \quad \text{(A1)}$$

where v is the transition frequency, n is the refractive index and χ_{ED} is the local-field correction for ED induced transitions with the form of $(n^2+1)^2/(9n)$ and $n(n^2+1)^2/9$ for absorption and emission transition, respectively. The Judd-Ofelt intensity parameters $\Omega_{(\lambda)}$ should be summed over λ=2,4,6 for a product with the even-rank reduced matrix elements of the $U^{(\lambda)}$ tensor operator.

The MD (A_{MD}) radiative decay rates can be written as[6-7]

$$A_{MD}=\frac{\pi he^2}{3\varepsilon_0c^5m_e^2}\frac{\nu^3}{g}\chi_{MD}\left|\left\langle l^N\psi\left\|L+g_eS\right\|l^N\psi'\right\rangle\right|^2 \quad \text{(A2)}$$

where g_e = 2.00232 is the gyromagnetic ratio of the electron and g is the degeneracy of the initial level. χ_{MD} is the local-field correction for MD induced transitions with the form of n and n^3 for the absorption and emission transition, respectively. ψ and ψ' are the statevectors for the initial and terminating levels for the $\psi \rightarrow \psi'$ transition, respectively. For transitions between J-multiplets, the statevector takes the form of $\psi(SLJ)$ with g = $(2J+1)$ while for transitions between crystal field levels, it takes the form of $\psi(SLJ\Gamma_i)$.

The radiative lifetime can be written as[6-7]

$$\tau_{SLJ} = \frac{1}{\sum_{S'L'J'} (A_{ED(SLJ \to S'L'J')} + A_{MD(SLJ \to S'L'J')})} \quad \text{(A3)}$$

The branching ratio can be written as[6-7]

$$\beta_{(SLJ \to S'L'J')} = \tau_{SLJ} \times [A_{ED(SLJ \to S'L'J')} + A_{MD(SLJ \to S'L'J')}] \quad \text{(A4)}$$

The MD absorption oscillator strengths can be written as[6-7]

$$P_{MD} = \frac{h\nu}{6m_e c^2} \frac{n}{(2J+1)} \left| \left\langle l^N SLJ \middle\| L + g_e S \middle\| l^N SLJ' \right\rangle \right|^2 \quad \text{(A5)}$$

Coordinates of all atoms for the optimized Nd:YAB

Atom	x	y	z
Nd	0.33352	0.33366	0.33355
Y	0.99963	0.00037	-0.00000
O 1	0.14654	0.55431	0.52959
O 3	0.47572	0.89045	0.85727
O 5	0.82035	0.21216	0.18730
O 7	0.29936	0.14631	0.52942
O 9	0.63397	0.47611	0.85709
O 11	0.96766	0.82062	0.18718
O 13	0.55401	0.29937	0.52920
O 15	0.89046	0.63362	0.85675
O 17	0.21179	0.96752	0.18707
O 19	-0.00001	0.14871	0.50004
O 21	0.00034	0.40989	0.49986
O 23	0.33180	0.48271	0.83595
O 25	0.33579	0.74080	0.83229
O 27	0.66846	0.81435	0.16408
O 29	0.66460	0.07636	0.16757
O 31	0.48287	0.18544	0.83594
O 33	0.74089	0.92321	0.83210
O 35	0.14864	0.85136	0.50000
O 36	0.40994	0.59006	0.50000
Al 1	0.00001	0.44555	0.99985
Al 3	0.33196	0.77766	0.33094
Al 5	0.66789	0.10988	0.66882
Al 7	0.77789	0.89019	0.33098
Al 9	0.44574	0.55426	0.00000
B 1	0.33347	0.33324	0.83504
B 3	0.00007	0.55881	0.50016
B 5	0.32992	0.89219	0.83516
B 7	0.66983	0.22227	0.16509
B 9	0.89230	0.77771	0.83491
B 11	0.00001	0.99999	0.50000
B 12	0.55868	0.44132	0.50000

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