

Supporting Information

Luminescence of Ce³⁺-Doped $M\text{B}_2\text{Si}_2\text{O}_8$ ($M = \text{Sr}, \text{Ba}$): a Deeper Insight into the Effects of Electronic Structure and Stokes Shift

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Calculation details of the CF analysis

The geometry structures of Ce^{3+} -doped $MB_2\text{Si}_2\text{O}_8$ optimized by the first-principles calculations were considered as an initial structural input to the ECM model considering the contribution from both the point- and exchange- charges to evaluate the 4f and 5d CF parameters (CFPs) of Ce^{3+} ions in the hosts. To ensure the sum convergence of the point-charge contribution over each crystal lattice ion, we generated a large cluster consisting of 26624 ions centered at Ce^{3+} site for each doped case. The charge value of each crystal lattice ion for the point-charge calculation can be taken from the Mulliken population analysis results given by the first-principles calculations. All the exchange charge parameters G_s , G_σ and G_π of each oxygen ligand around Ce^{3+} ions were simply approximated to a single value G . The G parameter for 4f electrons can be uniformly estimated as 9.65 for each oxygen ligand by following Ref.¹ due to the absence of the observed 4f-4f spectra of Ce^{3+} ions in $MB_2\text{Si}_2\text{O}_8$ for the 4f energy level fitting calculations, whereas the G parameter for 5d electrons can be kept the same for those oxygen ligands with the same Wyckoff notation, and thus only two parameters $G(\text{O}(8d))$ and $G(\text{O}(4c))$ are needed to be extracted from the 4f-5d excitation spectra of Ce^{3+} ions in $MB_2\text{Si}_2\text{O}_8$. The parameter α for the electrostatic correction to the second-order 4f and 5d CFPs was fixed and taken from our past work². Therefore, all the 4f and 5d CFPs can be evaluated in the framework of ECM and fed into the parameterized 4f and 5d CF Hamiltonian models with the fixed 4f and 5d spin-orbit coupling parameter values from Ref.³ to reproduce the observed 5d energy level structures of Ce^{3+} ions in $MB_2\text{Si}_2\text{O}_8$. All the 4f and 5d energy parameters used in the CF calculations were collected into [Table S2](#).

In addition to the energy level calculations, the 4f-5d electric-dipole transition intensities must be evaluated to characterize the intensities of the vibronic bands. These calculations can be done

very straightforward by employing Eq. (28) from the Ref.⁴ upon obtaining the wave functions of the 4f¹ and 5d¹ configurations by diagonalizing the effective parameterized Hamiltonian matrices for two configurations. For the simulation of the 4f-5d broad band structures, the model proposed by Reid et al.³ was adopted in our calculations, where the area beneath the absorption or emission band is proportional to the calculated 4f-5d transition intensity, and the broad bands are reproduced by using the Gaussian shaped curves with a full width at half maximum E_{width} , displaced from the zero-phonon lines (ZPLs) by E_{shift} . The absolute value of the parameter E_{shift} can be taken as a half of the Stokes shift derived from the energy difference between the lowest excitation maximum and the highest emission maximum of Ce³⁺ ions, and the positive E_{shift} is applied to the excitation spectrum whereas the negative one is for the emission spectrum. The value of the parameter E_{width} can be estimated from the first 4f-5d excitation band of Ce³⁺ ions. Here what we used are $E_{\text{shift}} = \pm 1130 \text{ cm}^{-1}$ and $E_{\text{width}} = 1500 \text{ cm}^{-1}$ for SrB₂Si₂O₈ and $E_{\text{shift}} = \pm 1200 \text{ cm}^{-1}$ and $E_{\text{width}} = 1600 \text{ cm}^{-1}$ for BaB₂Si₂O₈.

References:

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Table S1. Calculated and experimental structural data for pure $MB_2Si_2O_8$ ($M = Sr$ or Ba) crystals.

Coordinates of the crystallographic positions (in units of the lattice constants, (x, y, z) from top to bottom) of all ions are given. The symbol “ Z ” stands for the number of chemical formula units in one conventional unit cell.

<i>Pnma</i> (No. 62)	$SrB_2Si_2O_8$		$BaB_2Si_2O_8$	
	<i>Calc.</i>	<i>Exp.</i>	<i>Calc.</i>	<i>Exp.</i>
$a, \text{\AA}$	8.15650	8.155	8.15228	8.141
$b, \text{\AA}$	7.92264	7.919	8.21712	8.176
$c, \text{\AA}$	8.93821	8.921	9.05929	9.038
$\alpha=\beta=\gamma, {}^\circ$	90	90	90	90
$V, \text{\AA}^3$	577.59658	576.11	606.86684	601.58
Z	4	4	4	4
$M(4c)$	0.388696 0.250000 0.077687	0.38756 0.250 0.07841	0.387281 0.250000 0.083953	0.38853 0.250 0.08357
$B(8d)$	0.264255 0.081629 0.416204	0.2650 0.0808 0.4153	0.271220 0.086676 0.411078	0.2711 0.0855 0.4117
$Si(8d)$	0.060225 0.941865 0.191191	0.06105 0.94094 0.19163	0.073225 0.933123 0.189278	0.07232 0.93355 0.18988
$O1(8d)$	0.199450 0.985999 0.067132	0.2002 0.9833 0.0688	0.220829 0.951626 0.069886	0.2181 0.9538 0.07000
$O2(8d)$	0.132503 0.964924 0.360477	0.1344 0.9637 0.3597	0.145508 0.969973 0.354041	0.1458 0.9685 0.35401
$O3(8d)$	0.408455 0.073914 0.319669	0.4103 0.0725 0.3207	0.430060 0.065973 0.338762	0.4293 0.0653 0.3369
$O4(4c)$	0.491781 0.750000 0.328200	0.4924 0.750 0.3277	0.495370 0.750000 0.311240	0.4966 0.750 0.3126
$O5(4c)$	0.194570 0.250000 0.415805	0.1951 0.250 0.4127	0.210205 0.250000 0.377901	0.2083 0.250 0.3807

Table S2. The 4f and 5d energy parameters of Ce³⁺ ions doped in $MB_2Si_2O_8$ ($M = Sr$ and Ba) in the framework of ECM (unit: cm⁻¹).

	SrB ₂ Si ₂ O ₈		BaB ₂ Si ₂ O ₈	
	4f	5d	4f	5d
B_0^2	94	-2180	91	-1256
B_1^2	-324+48 <i>i</i>	-687-415 <i>i</i>	-314-45 <i>i</i>	-1969+344 <i>i</i>
B_2^2	-463+62 <i>i</i>	3136-550 <i>i</i>	-326-54 <i>i</i>	2761+410 <i>i</i>
B_0^4	335	6676	151	5677
B_1^4	-24-5 <i>i</i>	941-74 <i>i</i>	114+4 <i>i</i>	5890+60 <i>i</i>
B_2^4	-1655-1 <i>i</i>	-20918-20 <i>i</i>	-745+1 <i>i</i>	-16522+13 <i>i</i>
B_3^4	265-1 <i>i</i>	3457-22 <i>i</i>	169+1 <i>i</i>	4352+21 <i>i</i>
B_4^4	78-6 <i>i</i>	1716-91 <i>i</i>	225+4 <i>i</i>	5288+71 <i>i</i>
B_0^6	-1188		-619	
B_1^6	-82		-100	
B_2^6	-485		-227	
B_3^6	256		297	
B_4^6	554		212	
B_5^6	-109		-156	
B_6^6	639		401	
ξ	614.9	1082	614.9	1082
E_{avg}	1598		1452	
$\Delta_E(fd)$		[35950]		[35020]
$G(O(4c))$	9.65	[2.2470]	9.65	[3.6301]
$G(O(8d))$	9.65	[1.2754]	9.65	[2.1531]
α	-1.09	-1.76	-1.09	-1.76

Note: The parameter values in the brackets were optimized by fitting the experimental 5d energy levels.

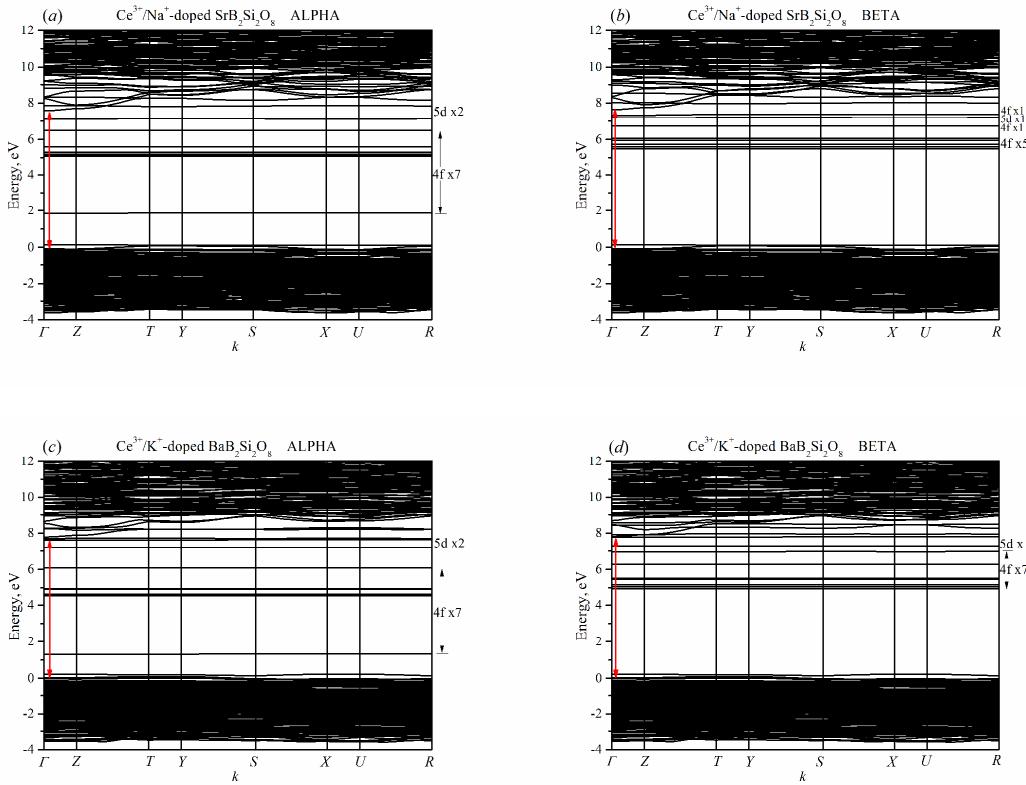


Figure S1. Calculated band structure diagrams for Ce³⁺/Na⁺-doped SrB₂Si₂O₈ (a, b) and Ce³⁺/K⁺-doped BaB₂Si₂O₈ (c, d) crystals. Those red two-way arrows are used to indicate the energy separation between the host valence and conduction bands. The letters Γ , Z, T, Y, S, X, U and R represent the high-symmetry k points (0,0,0), (0,0,1/2), (0,1/2,1/2), (0,1/2,0), (1/2,1/2,0), (1/2,0,0), (1/2,0,1/2) and (1/2,1/2,1/2), respectively. The symbols “ALPHA” and “BETA” represent the electronic pictures with the up and down spins, respectively.

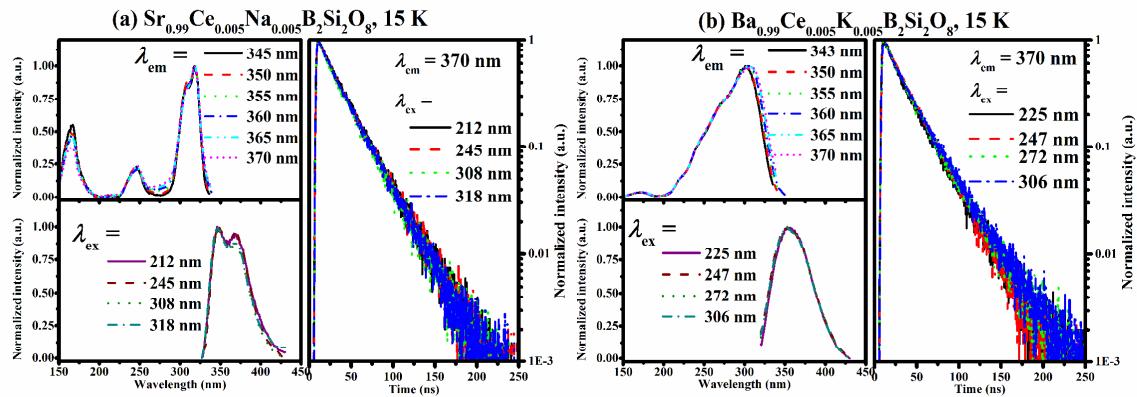


Figure S2. Excitation spectra under different emission wavelengths, emission spectra under different excitation wavelengths, luminescence decay curves under different excitation wavelengths and the same emission wavelength of $\text{Sr}_{0.99}\text{Ce}_{0.005}\text{Na}_{0.005}\text{B}_2\text{Si}_2\text{O}_8$ (a) and $\text{Ba}_{0.99}\text{Ce}_{0.005}\text{K}_{0.005}\text{B}_2\text{Si}_2\text{O}_8$ (b) at 15 K.

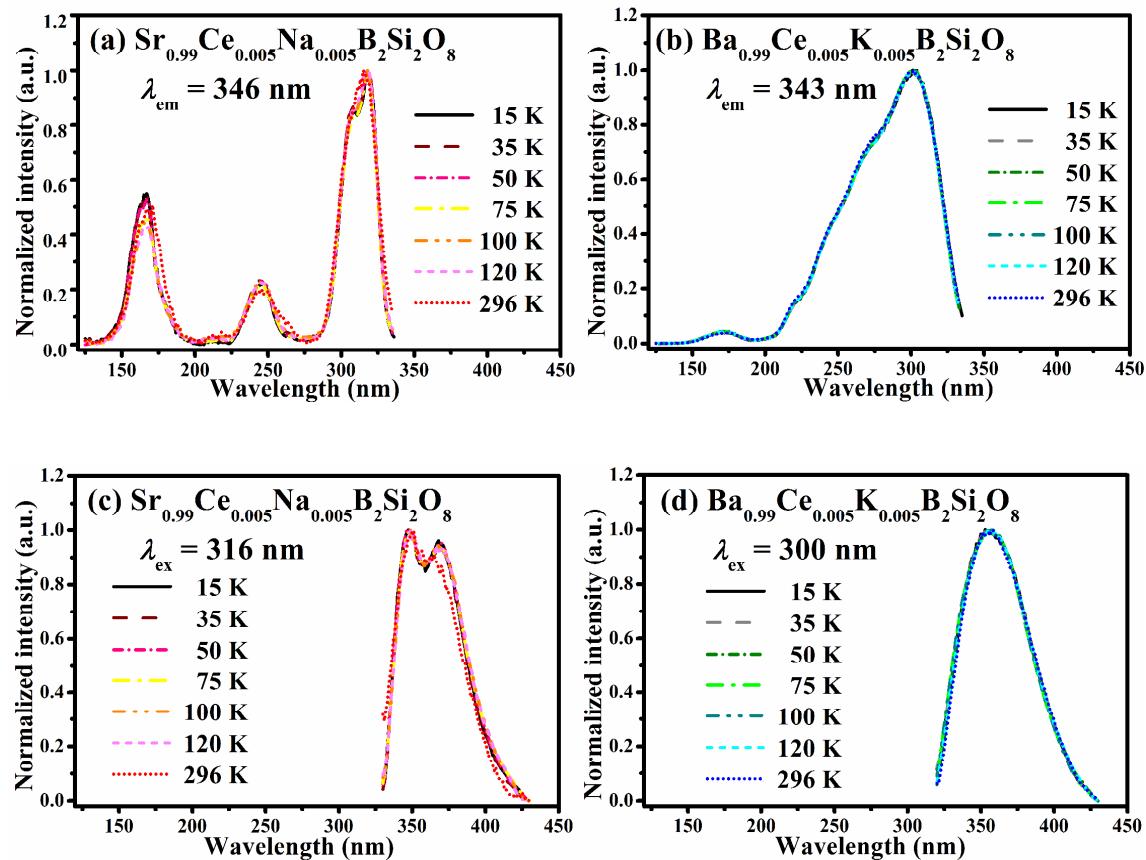


Figure S3. Temperature-dependent excitation and emission spectra of $\text{Sr}_{0.99}\text{Ce}_{0.005}\text{Na}_{0.005}\text{B}_2\text{Si}_2\text{O}_8$ (a, c) and $\text{Ba}_{0.99}\text{Ce}_{0.005}\text{K}_{0.005}\text{B}_2\text{Si}_2\text{O}_8$ (b, d).

Full authors of reference (22)

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