First-Principles Study on Structural, Electronic, and Spectroscopic Properties of γ-Ca_2SiO_4: Ce^{3+} Phosphors

Jun Wen,[a,*] Lixin Ning,[b] Chang-Kui Duan,[c] Shengbao Zhan,[a] Yucheng Huang,[b] Jie Zhang,[a] and Min Yin[c]

[a] *School of Physics and Electronic Engineering, Anqing Normal University, Anqing 246011, People's Republic of China*

[b] *Center for Nano Science and Technology, Department of Physics, Anhui Normal University, Wuhu 241000, People's Republic of China*

[c] *Department of Physics, University of Science and Technology of China, Hefei 230026, People's Republic of China*

* Corresponding author. E-mail: wenjunkd@mail.ustc.edu.cn. Telephone: +86-15855154475 (J. W.).

Table S1. DFT-optimized and experimentally measured lattice parameters for undoped and Ce-doped γ-Ca_2SiO_4 (for the substitutions with the neighboring oxygen vacancies around the Ce^{3+}).

Method	2*a* (Å)	*b* (Å)	2*c* (Å)	*α* (deg)	*β* (deg)	*γ* (deg)
Exptl.[a]	10.156	11.225	13.520	90.000	90.000	90.000
Undoped	10.248	11.340	13.619	90.000	90.000	90.000
$Ce_{Ca1}^{\bullet}$-$V_{O1b}^{\bullet\bullet}$	10.321	11.368	13.632	89.842	89.930	89.930
$Ce_{Ca1}^{\bullet}$-$V_{O2a}^{\bullet\bullet}$	10.274	11.395	13.640	89.872	89.944	89.949
$Ce_{Ca1}^{\bullet}$-$V_{O3b}^{\bullet\bullet}$	10.317	11.373	13.652	89.644	89.766	90.354
$Ce_{Ca1}^{\bullet}$-$V_{O4a}^{\bullet\bullet}$	10.330	11.381	13.650	90.255	90.301	90.447
$Ce_{Ca1}^{\bullet}$-$V_{O5a}^{\bullet\bullet}$	10.324	11.375	13.660	89.595	90.225	89.888
$Ce_{Ca2}^{\bullet}$-$V_{O1}^{\bullet\bullet}$	10.326	11.368	13.598	90.000	90.000	89.769
$Ce_{Ca2}^{\bullet}$-$V_{O2a}^{\bullet\bullet}$	10.321	11.372	13.619	89.728	89.839	90.118
$Ce_{Ca2}^{\bullet}$-$V_{O3b}^{\bullet\bullet}$	10.324	11.384	13.610	90.315	89.814	89.773
$Ce_{Ca2}^{\bullet}$-$V_{O4}^{\bullet\bullet}$	10.284	11.395	13.608	89.917	89.986	89.958
$Ce_{Ca2}^{\bullet}$-$V_{O6a}^{\bullet\bullet}$	10.292	11.389	13.593	90.069	89.991	89.946

[a] Ref 30.

Table S2. DFT-optimized Ca^{2+}-O^{2-} and Ce^{3+}-O^{2-} (in the substitutions with the neighboring oxygen vacancies around the Ce^{3+}) bond lengths (in Å) in the undoped and Ce-doped γ-Ca_2SiO_4.

Site 1	M = Ca1	M = Ce_{Ca1}				
		$Ce_{Ca1}^{\bullet}$-$V_{O1b}^{\bullet\bullet}$	$Ce_{Ca1}^{\bullet}$-$V_{O2a}^{\bullet\bullet}$	$Ce_{Ca1}^{\bullet}$-$V_{O3b}^{\bullet\bullet}$	$Ce_{Ca1}^{\bullet}$-$V_{O4a}^{\bullet\bullet}$	$Ce_{Ca1}^{\bullet}$-$V_{O5a}^{\bullet\bullet}$
M-O1a	2.3242	2.2501 (−0.0741)	2.2247 (−0.0995)	2.2762 (−0.0480)	2.3325 (+0.0083)	2.3567 (+0.0325)
M-O1b	2.3242	−	2.2177 (−0.1065)	2.3650 (+0.0408)	2.3871 (+0.0629)	2.3797 (+0.0555)
M-O2a	2.3847	2.2190 (−0.1657)	−	2.2290 (−0.1557)	2.4247 (+0.0400)	2.2825 (−0.1022)
M-O2b	2.3847	2.3327 (−0.0520)	2.2880 (−0.0967)	2.3627 (−0.0220)	2.3773 (−0.0074)	2.4170 (+0.0323)
M-O3a	2.4132	2.2418 (−0.1714)	2.2300 (−0.1832)	2.2844 (−0.1288)	2.4422 (+0.0290)	2.4237 (+0.0105)
M-O3b	2.4132	2.3854 (−0.0278)	2.2516 (−0.1616)	−	2.3954 (−0.0178)	2.4197 (+0.0065)
Site 2	M = Ca2	M = Ce_{Ca2}				
		$Ce_{Ca2}^{\bullet}$-$V_{O1}^{\bullet\bullet}$	$Ce_{Ca2}^{\bullet}$-$V_{O2a}^{\bullet\bullet}$	$Ce_{Ca2}^{\bullet}$-$V_{O3b}^{\bullet\bullet}$	$Ce_{Ca2}^{\bullet}$-$V_{O4}^{\bullet\bullet}$	$Ce_{Ca2}^{\bullet}$-$V_{O6a}^{\bullet\bullet}$
M-O1	2.3130	−	2.2002 (−0.1128)	2.3139 (+0.0009)	2.2438 (−0.0692)	2.1927 (−0.1203)
M-O2a	2.3964	2.1825 (−0.2139)	−	2.2752 (−0.1212)	2.1860 (−0.2104)	2.3951 (−0.0013)
M-O2b	2.3964	2.1825 (−0.2139)	2.3097 (−0.0867)	2.2115 (−0.1849)	2.3742 (−0.0222)	2.2507 (−0.1457)
M-O3a	2.4506	2.4469 (−0.0037)	2.4280 (−0.0226)	2.3480 (−0.1026)	2.2822 (−0.1684)	2.2820 (−0.1686)
M-O3b	2.4506	2.4469 (−0.0037)	2.3095 (−0.1411)	−	2.3184 (−0.1322)	2.3001 (−0.1505)
M-O4	2.4719	2.3324 (−0.1395)	2.3242 (−0.1477)	2.4284 (−0.0435)	−	2.4357 (−0.0362)

Table S3. Calculated energies (in cm^{-1}) of the 4f states for the Ce^{3+} with the neighboring oxygen vacancy $V_O^{\bullet\bullet}$ (i.e., the $Ce_{Ca}^{\bullet}$-$V_O^{\bullet\bullet}$ substitutions).

Levels	$Ce_{Ca1}^{\bullet}$-$V_O^{\bullet\bullet}$					$Ce_{Ca2}^{\bullet}$-$V_O^{\bullet\bullet}$					
	V_{O1b}	V_{O2a}	V_{O3b}	V_{O4a}	V_{O5a}	V_{O1}	V_{O2a}	V_{O3b}	V_{O4}	V_{O5}	V_{O6a}
$4f_1$	0	0	0	0	0	0	0	0	0	0	0
$4f_2$	1217	2191	541	883	636	1430	668	995	735	1276	2015
$4f_3$	2541	3495	820	1174	1191	2342	2192	2089	1022	1764	2896
$4f_4$	3027	4687	2483	2272	2261	3014	2556	2785	2203	2338	3922
$4f_5$	3507	6773	2896	2986	2831	3821	2819	3229	3054	3614	5017
$4f_6$	5012	8361	3486	3496	3417	4806	4575	4517	4490	4253	5295
$4f_7$	6439	8697	5302	3917	3852	6534	5908	5665	7576	4590	6135

Table S4. Calculated energies (in cm^{-1}) of the 4f states for the clusters $(Ce_{Ca1}O_6)^{9-}$ and $(Ce_{Ca2}O_6)^{9-}$ embedded in the γ-Ca_2SiO_4.

Levels	$Ce_{Ca1}^{\bullet}$	$Ce_{Ca2}^{\bullet}$	$Ce_{Ca1}^{\bullet}$-Al_{Si}'	$Ce_{Ca2}^{\bullet}$-Al_{Si}'	$Ce_{Ca1}^{\bullet}$-V_{Ca}''	$Ce_{Ca2}^{\bullet}$-V_{Ca}''
$4f_1$	0	0	0	0	0	0
$4f_2$	1044	812	1123	819	1019	810
$4f_3$	1484	1106	1336	1119	1494	1292
$4f_4$	2395	2243	2358	2244	2407	2279
$4f_5$	3215	2885	3126	3002	3194	3012
$4f_6$	4053	3287	3783	3244	3930	3298
$4f_7$	4398	3936	4217	3516	4279	4109