Assessment of First-Principles and Semiempirical Methodologies for Absorption and Emission Energies of Ce³⁺-Doped Luminescent Materials

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In search of a reliable methodology for the prediction of light absorption and emission of Ce³⁺-doped luminescent materials, 13 representative materials are studied with first-principles and semiempirical approaches. In the first-principles approach, that combines constrained density-functional theory and ΔSCF, the atomic positions are obtained for both ground and excited states of the Ce³⁺ ion. The structural information is fed into Dorenbos' semiempirical model. Absorption and emission energies are calculated with both methods and compared with experiment. The first-principles approach matches experiment within 0.3 eV, with two exceptions at 0.5 eV. In contrast, the semiempirical approach does not perform as well (usually more than 0.5 eV error). The general applicability of the present first-principles scheme, with an encouraging predictive power, opens a novel avenue for crystal site engineering and high-throughput search for new phosphors and scintillators.

The $4f \rightarrow 5d$ transition of Ce³⁺ ion has been widely used in the design of efficient luminescent systems such as white light-emitting diode (LED) phosphors, scintillators, and laser materials due to its spin-allowed character and its tunability as a function of the host material.[1,4–8] Until now, most of the efforts to find new hosts relied on trial and error. An accurate and efficient methodology to design new materials would be a remarkable achievement. With this idea in mind, a semiempirical model has been proposed by Dorenbos, to describe Ce³⁺

luminescence in inorganic compounds.[9] This semiempirical model provides correct general trend for absorption. Unfortunately, it suffers from several drawbacks. First, its quantitative predictions rely on some fitting parameters, which have been determined only for oxide, nitride, and fluoride materials at present.[8] Second, the semiempirical model fails to predict the emission energy and Stokes shift. This limitation is due to missing experimental relaxed structure configurations in the excited state. These two shortcomings result in limited accuracy and scope of the semiempirical approach.

In a recent paper, we have explored a first-principles alternative to overcome the drawbacks of Dorenbos' semiempirical model.[10] The successful quantitative description of the neutral excitation, emission energy, and Stokes shift in two Ce³⁺-doped lanthanum silicate nitrides has been realized. Our approach is based on constrained density functional theory (CDFT) and the ΔSCF (SCF: Self-Consistent Field) methods, following the early work by Marsman et al.[11] Recently, Canning et al. used CDFT to identify several promising hosts for efficient scintillators, but they did not study the emission and Stokes shifts.[12] In the present work, we assess the generality and accuracy of the proposed theoretical method and compare it with Dorenbos' semiempirical model. To do so, first we study from first principles the absorption, emission, and Stokes shift of a set of 13 representative Ce³⁺-doped materials that include oxides, nitrides, and halides, and that span a large range of transition energies, from 2 to 5 eV. Then, the first-principles structural characterization of the ground state as well as the excited state is fed into the Dorenbos' semiempirical model. Finally, experimental transition energies and Stokes shift are compared to the ab initio simulation and semiempirical model to assess their accuracy and generality.

Detailed information about the Dorenbos' semiempirical model and theoretical method can be found in the Supporting Information. The calculations in this work were performed within density functional theory (DFT) as implemented in the ABINIT package.[13–15] Still, DFT is a ground-state theory and its generalization to the excited state description thanks to CDFT does not benefit from a strong theoretical basis. The present work is thus justified by the comparison with experimental data. **Figure 1** shows the electron occupancy in CDFT. The excited state of the Ce³⁺ ion is obtained by constraining the very

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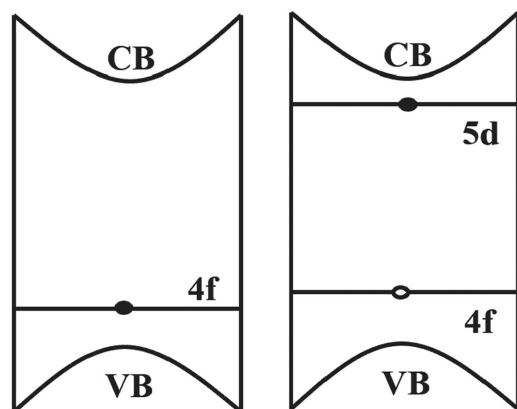
Figure 1. Electron occupation of the levels inside the host band gap, in the ground state and excited state.

localized predominantly 4f bands to be unoccupied, while occupying the lowest state lying higher in energy (for most cases, this state is identified afterward to be a localized 5d state of the Ce^{3+} ion). Total energy differences (ΔSCF) between the ground state and such excited state will be associated to the energy change due to photon absorption and emission. The absorption and emission energy are determined at the relaxed geometry of the electronic ground and excited state, respectively, which corresponds to Figure S1 of the Supporting Information.

Table 1 shows the transition energy and Stokes shift from our first-principles calculations and from experimental data for the 13 representative Ce^{3+} ion doped materials. The details on the geometry optimization and band structure results for all the compounds are reported in the Supporting Information. **Figure 2**a–c compares first-principles and experimental

results. In general, the experimental and computed values for absorption and emission energies are within 0.3 eV of each other, although in two cases, the agreement is at the level of 0.5 eV. First-principles Stokes shifts are within 30% of the experimental data, with one exception at 50%. The results for $LiYSiO_4$:Ce and LaF_3:Ce are less satisfactory than in other materials and might perhaps be associated with the very light Li atom (vibrational effect) and strongly electronegative F atom. Apart from these two materials, we deduce that: (1) the first-principles methodology can successfully describe oxide-, nitride-, and halide-based phosphors, with absorption and emission energies in the region of 2–5 eV; (2) the atomic geometry of ground and excited states for the Ce^{3+}-doped materials is reasonably well described. This highlights the potential of such first-principles approach for the high-throughput design of novel Ce^{3+}-based optical materials. Also, such first-principles approach can provide a theoretical insight into the crystal-site engineering approach, which has been recently proposed from experiment to tune the luminescence of rare earth doped phosphors.[23] Indeed, the luminescent center in Ce^{3+} doped phosphor has been directly identified from our ab initio method as the crystal site leading to the lowest Ce_{5d} state in the bandgap of the host material.

Based on the obtained structural geometry, we extend the scope of the Dorenbos' semiempirical model from absorption analysis to the prediction of emission energy and Stokes shift. Relying on the semiempirical redshift D(A) computed for the ground and excited structural geometry, the absorption and emission energy can be defined as

$$E(A) = 49\,340\,cm^{-1} - D(A) \tag{1}$$

In this equation, 49 340 cm^{-1} is the energy of the first 4f → 5d transition of Ce^{3+} as a free (gaseous) ion. Stokes shift values can then be calculated as the difference between absorption and emission energies. Here, 11 compounds (oxides,

Table 1. Absorption (Abs, eV), emission (Em, eV) energy, and Stokes shift ΔS (cm^{-1}), from first-principles calculations and experiment for 13 Ce^{3+} doped host materials. Only few numbers in bold deviate substantially from experiment.

Compounds	First-principles			Experiment			
	Abs	Em	ΔS	Abs	Em	ΔS	Reference
$La_3Si_6N_{11}$:Ce	2.79	2.40	3160	2.58	2.25	2717	[16]
$Ce_3Si_6N_{11}$	2.81	2.42	3146	2.63	2.26	2974	[17]
$Y_3Al_5O_{12}$:Ce	2.78	2.36	3424	2.67	2.30	2984	[18]
$Lu_3Al_5O_{12}$:Ce	2.94	2.59	2823	2.77	2.48	2339	[18]
$CeSi_3N_5$	3.60	3.19	3307	3.35	2.88	3791	[19]
$LaSi_3N_5$:Ce	3.50	3.12	3080	3.43	2.95	3815	[20]
$LiYSiO_4$:Ce	**4.02**	3.33	**5575**	3.54	3.10	3740	[21]
$Lu_2Si_2O_7$:Ce	3.88	3.57	2480	3.55	3.27	2258	[22]
$LaBr_3$:Ce	3.92	3.52	3226	4.03	3.48	4439	[23]
$YAlO_3$:Ce	4.14	3.56	4678	4.09	3.59	4033	[7a]
$LaCl_3$:Ce	4.37	3.86	4113	4.41	3.70	5762	[22]
$LaPO_4$:Ce	4.84	4.30	4355	4.51	3.91	4818	[7a]
LaF_3:Ce	**5.38**	**4.74**	5162	4.98	4.34	5162	[7b]

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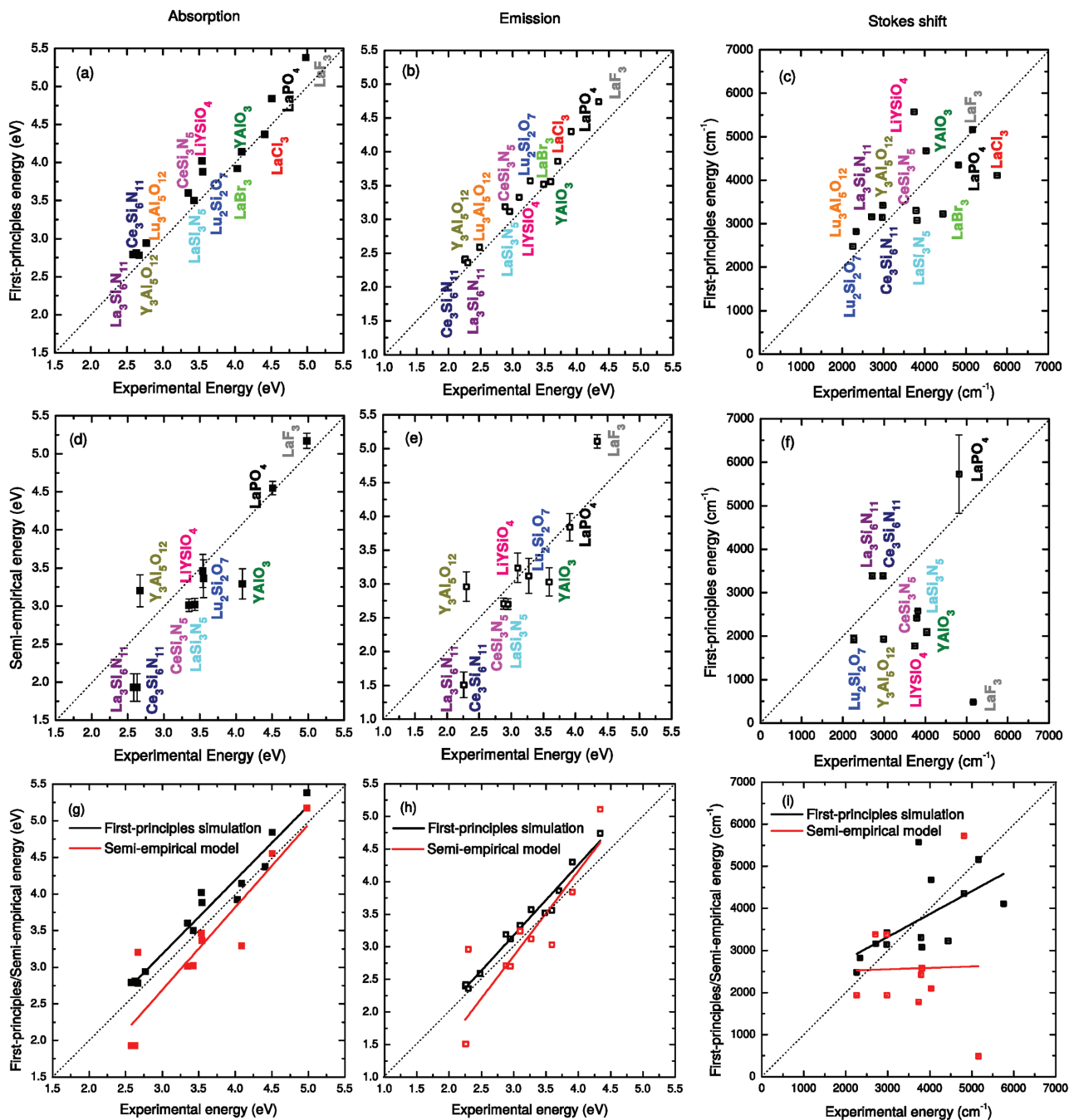MATERIALS
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Figure 2. Comparison between experimental results and first-principles calculations: a) absorption, b) emission, and c) ΔS; between experimental results and semiempirical model for d) absorption, e) emission, and f) ΔS, g) fitting line of absorption energy, h) fitting line of emission energy, and i) fitting line of ΔS. The error bars for the semiempirical model stem from the low and high limits of the crystal-field splitting.

nitrides, and one fluoride), among the 13 materials used for the first-principle study, for which the spectroscopic polarization α_{sp} is available, have been selected for this analysis. The information needed for the determination of the redshift, $D(A)$, is listed in the Supporting Information. We consider the lowest and highest limits for the contribution from the crystal field splitting. The average of the high and low-limit results is compared with experiment in Figure 2d–f while the error bar stands for the low and high limits in the extended semiempirical

approach. The fitting result for $Lu_3Al_5O_{12}$:Ce was not included in these figures because its Stokes shift is negative.

Figure 2g–i shows the comparison between first-principles calculation and semiempirical model. A statistical analysis was performed to find the linear relationship between experiment and predictive models. The detailed analysis is given in **Table 2**. From these results, it can be concluded that, in the present domain of applicability of the Dorenbos' semiempirical model, the first-principles approach gives generally more

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Table 2. Statistical analysis of transition energy and Stokes shift from first-principles calculation and semiempirical model. ME (eV, cm^{-1}), MAE (eV, cm^{-1}), MRE (%), and MARE (%) stand for the mean error, mean absolute error, mean relative error, and mean absolute relative error, respectively. The slope, intercept, and coefficient of determination (R^2) correspond to the linear fitting in Figure 2g–i. The most problematic quantities are indicated in bold.

	First-principles			Semiempirical		
	Abs	Em	ΔS	Abs	Em	ΔS
ME	0.175	0.205	33.5	−0.118	0.027	**−1118**
MAE	0.205	0.210	**728**	0.350	0.423	**1502**
MRE	5.100	6.280	4.17	3.540	−0.01	**−26.7**
MARE	5.850	6.410	**19.1**	**10.8**	**14.6**	**37.3**
Slope	1.010	1.080	0.543	1.13	1.30	**0.033**
Intercept	0.142	−0.066	1677	−0.713	−1.041	2453
R^2	95.1	97.1	33.3	81.4	76.6	**−12.4**

accurate optical transition energies and Stokes shift. Actually, the first-principles transition energies and Stokes shift can be further corrected based on the statistical analysis parameters, namely slope and intercept of the linear fit between first-principle calculation and experiment. The results are shown in the Supporting Information, which give all the corrected transition energy matching the experiment within 0.3 eV. On the other hand, the predictive power of the semiempirical method is limited by the following factors. First, the semiempirical method provides a negative Stokes shift for Lu$_3$Al$_5$O$_{12}$:Ce, in contradiction to experiment. Second, the semiempirical method cannot provide a correct trend for the Ce^{3+} emission in LaSi$_3$N$_5$ and Y$_3$Al$_5$O$_{12}$. Both issues are solved in our ab initio approach.

In summary, we analyzed the luminescence in 13 different Ce^{3+}-doped materials using first-principles calculations and a semiempirical model. The obtained results show that the first-principles approach, based on CDFT and the ΔSCF method, can accurately describe the neutral excitations in these materials and gives transition energies and Stokes shift that are generally within 0.3 eV and 30% (with two exceptions at 0.5 eV and 50%) of the experimental data, respectively. The general applicability of this method has been validated and can be used in high-throughput computational screening and crystal-site engineering of novel luminescent systems. The quantitative analysis based on Dorenbos' semiempirical model is limited in its generality and is less accurate than the first-principles approach. Such limitation might be ascribed to the fact that only structural information is explicitly taken into account in the semiempirical model while the details of the electrostatic, exchange, and correlation energies, linked to the (de)localization of the occupied 5d electronic level in the excited state should have an important effect on the luminescence, which is reasonably described in our first-principles calculations. We think that the latter argument explains the intriguing agreement of the CDFT and ΔSCF approach with experiment.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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