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Luminescence properties of $\text{Al}_2\text{O}_3:\text{Ti}$ in the blue and red regions: a combined theoretical and experimental study

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Abstract

Using on jointly experimental results and first-principles calculations, we unambiguously assign the underlying mechanisms behind two commonly observed luminescence bands for the Al_2O_3 material. Indeed, we show that the red band is associated with a Ti^{3+} $d-d$ transitions as expected, while the blue band is the combination of the $\text{Ti}^{3+} + \text{O}^- \rightarrow \text{Ti}^{4+} + \text{O}^{2-}$ and $\text{V}_\text{O}^\bullet + e^- \rightarrow \text{V}_\text{O}^\times$ deexcitation processes. Thanks to our last developments which take into account the vibrational contributions to the electronic transitions in solids, we were able to simulate the luminescence spectra for the different signatures. The excellent agreement with experiment demonstrates that it should be possible to predict the color of the material with a CIE chromaticity diagram. We also anticipated the luminescence signature of $\text{Al}_2\text{O}_3:\text{Ti,Ca}$ and $\text{Al}_2\text{O}_3:\text{Ti,Be}$ that were confirmed by experiment.

13 Introduction

14 Aluminum oxide (Al_2O_3) is recognized for its exceptional versatility and resilience, attributed
15 to a unique combination of properties. With a melting point of 2072 degrees Celsius, sig-
16 nificantly surpassing that of most metals and ceramics, it is a preferred material for high-
17 temperature applications. A hardness rating of 9 on the Mohs scale endows it with remark-
18 able resistance to wear. Its low electrical conductivity qualifies it as an effective insulator,
19 complemented by superior wear resistance, ensuring durability in demanding environments.
20 Noteworthy is its unwavering chemical stability, guaranteeing structural integrity even in the
21 presence of harsh chemicals and extreme conditions. These distinctive properties establish
22 Al_2O_3 as a prominent and widely utilized material.¹⁻¹²

23 The natural form of alumina ($\alpha\text{-Al}_2\text{O}_3$), called corundum, is also known for its optical
24 properties. Intrinsically colorless due to a very large band gap (≈ 9 eV), the presence of
25 numerous «extrinsic» impurities (in a lesser extent intrinsic one) may lead to the appearance
26 of absorption bands in the visible range.¹³ Thus, the hue of Al_2O_3 could range from blue
27 thanks to a $\text{Fe}^{2+} + \text{Ti}^{4+} \rightarrow \text{Fe}^{3+} + \text{Ti}^{3+}$ to red or green in presence of Cr^{3+} due to on-site
28 $d-d$ transition.^{14,15} Many samples have also been described as luminescent, in that case the
29 origin of the observed emissions being related to intrinsic and extrinsic defects.^{2,16,17}

30 Among all the dopants, Al_2O_3 may naturally contain titanium, and the intense evolution
31 of alumina doping techniques has led to the creation of lasers labeled $\text{Al}_2\text{O}_3:\text{Ti}$.¹⁸⁻²⁰ In that
32 case, a luminescence band appears between 700 and 770 nm (*i.e.* 1.77 and 1.61 eV) and is
33 unambiguously assigned to a Ti^{3+} $d-d$ on-site transition.²¹⁻²⁴

34 A second band in the blue region, with a maximum around 430 nm (2.88 eV), has also
35 been observed in Ti-based laser.¹⁶ Unlike the red one, this luminescence generated many
36 theories but no definitive proof has yet been established to certify its origin(s). Indeed, this
37 emission was successively assigned to the presence of F centers (a neutral defect made of an
38 oxygen vacancy with two trapped electrons), to Ti^{4+} with a possible presence of a +II cation
39 (*e.g.* Mg^{2+}).^{22,25-45}

40 However, despite numerous studies, the origin of the blue luminescence band is still un-
41 certain. It is at this point that theoretical calculations must play a pivotal role. Nevertheless,
42 despite the intense development of new theoretical calculation techniques, one could not fully
43 assess the Ti-related luminescence properties in Al_2O_3 so far, even though some electronic
44 transitions (through defect formation enthalpies computations) and defect formation ener-
45 gies are known.⁴⁶⁻⁵⁷ The luminescence properties are still challenging to model and up to
46 now nobody succeeded in simulating simultaneously the red and the blue luminescence sig-
47 natures with a good accuracy. In this article, we draw upon recent computational techniques
48 that we have developed with the aim of simulating luminescence. Indeed, we were able (i)
49 to get insights of the structure of the excited state (ES) and to get the luminescence energy
50 of the $\text{ZrO}_2\text{:Ti}$ material,⁵⁸ and (ii) to simulate the full luminescence spectrum including the
51 vibrational contributions to the electronic transition of $\text{BaZrO}_3\text{:Ti}$.⁵⁹ Herein, we simulated
52 both aforementioned luminescence signatures, *i.e.* the red one from Ti^{3+} and the blue one,
53 which was still under debate. In this paper, we provide a definitive answer concerning the
54 origin of the observed blue band thanks to state-of-the-art modeling in solids. Moreover,
55 our model predicts the fine tuning of the blue luminescence band depending on the +II
56 charge compensating cation, which was subsequently confirmed using chemical syntheses
57 and characterizations.

58 **Methods**

59 **Experimental details**

60 Luminescence spectra were collected on five distinct $\text{Al}_2\text{O}_3\text{:Ti}$ samples:

- 61 • one synthetic Verneuil monocrystal (hereafter labeled **I**) was purchased from the com-
62 pany Djevahirdjian scientific stones (Switzerland),
- 63 • one natural gemstone (hereafter labeled **II**) from Sri Lanka was acquired through Astrid

64

Corporation (Hong Kong),

65

- one synthetic powder sample with Ti+Mg codoping (hereafter labeled **III**) was prepared for this study (see SI for details),

66

67

- one synthetic powder sample with Ti+Ca codoping (hereafter labeled **IV**) was prepared for this study,

68

69

- one natural sample (hereafter labeled **V**) treated with Be diffusion technique also purchased to Astrid Corporation (Hong Kong).⁶⁰

70

71

Traces elements were identified and quantified for all samples via LA-ICP-MS analyses

72

(see SI). Major detected elements are summed up in Table 1.

Table 1: ICP-MS elemental analysis on natural and synthetic Al₂O₃ samples. *bld* stands for below limits of detection.

	⁴⁷ Ti (ppm)	²⁴ Mg (ppm)	⁹ Be (ppm)	⁴⁴ Ca (ppm)
I	468	5	<i>bld</i>	<i>bld</i>
II	305	118	<i>bld</i>	<i>bld</i>
III	3910	1822	1	<i>bld</i>
IV	3085	525	<i>bld</i>	8462
V	114	556	1437	1647

73

The spectroscopic data were acquired with a Horiba JobinYvon Fluorolog-3 fluorimeter.

74

The collect of emission spectra were carried out in the 300 to 900 nm range (1.37 to 4.13 eV)

75

with an excitation at 254 nm. For Raman spectrum recording, an ultrapure sample Al₂O₃

76

(hereafter labeled **VI**) loaned from Daniel Ritz at Spolchemie (Czech Republic) was used.

77

Raman scattering spectra were obtained on a Jobin Yvon T64000 spectrometer with a 514

78

nm Ar-laser (see SI).

79

Computational details

80

Structures and electronic structures of the ground and excited states computations were

81

performed with the plane wave software VASP with the GGA functional PBE, using the

82 projector augmented wave formalism and a cutoff energy of 550 eV.^{61–64} For the vibrational
83 properties, the CRYSTAL17 software was used with the global hybrid PBE0 functional for
84 the bulk, and the PBE functional for the faulted cell, together with the DZVP Rev2 basis
85 set after a proper geometrical relaxation.^{65–67}

86 **Bulk computations** The host structure was studied on the 10 atoms primitive cell (rhom-
87bohedral setting of the regular $R\bar{3}c$ trigonal cell with $Z = 2$). For the structural relaxation,
88 the first Brillouin zone was paved of a $10 \times 10 \times 10$ k-mesh Monkhorst-Pack grid and forces
89 were optimized under $5.0 \cdot 10^{-3}$ eV/Å. For accurate energy computations, the Brillouin zone
90 was paved of a $13 \times 13 \times 13$ k-mesh Γ -centered grid and the residual of total energy was
91 converged under 10^{-7} eV. For the vibrational computation, 5761 k-points and a convergence
92 on the energy of 10^{-10} eV were used.

93 **Al₂O₃:V_O and Al₂O₃:Ti(,M) ground and excited states (M= Mg, Ca and Be)**

94 The doped and co-doped Al₂O₃ were investigated using supercells of 120 atoms ($2 \times 2 \times 1$
95 with respect to the conventional trigonal cell). For these structures, only the atomic positions
96 were allowed to relax, the volume being kept identical to the pure material in order to model
97 diluted defect. Forces and energies were converged under 10^{-2} eV/Å and under 10^{-7} eV,
98 respectively providing the coordinates and energy in the electronic ground state (point **A**
99 from Figure 1). Excited state structures were relaxed using the so-called constrained DFT
100 (cDFT) which allows one to specify an arbitrary electronic occupation of Kohn-Sham bands.
101 The relaxation and energy computation with cDFT yields the energy and atomic positions of
102 the most stabilized electronic state in the excited configuration (point **C** of Figure 1). These
103 atomic positions are then used unrelaxed to compute the energy of point **D**. The energy
104 difference between **C** and **D** is used here as the Electronic Vertical Transition energy. This
105 method has already been used successfully in a previous study dealing with the luminescence
106 properties of ZrO₂ and BaZrO₃ doped with titanium.^{58,59} It is also a very well-known method
107 in molecular simulation, which allows one to accurately predict the luminescence color of

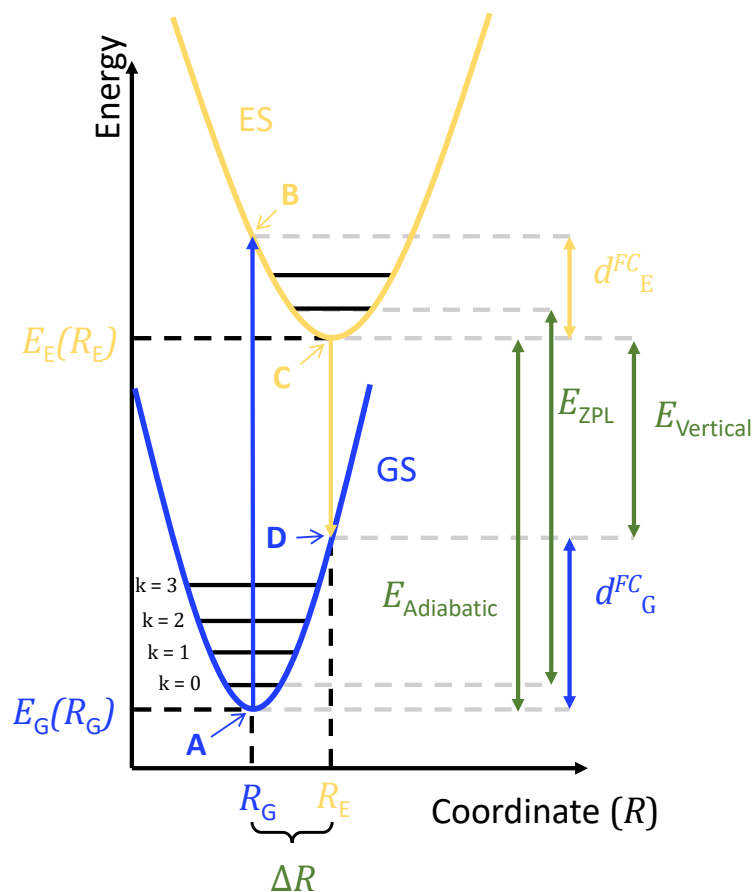


Figure 1: Schematic representation of the luminescence process with characteristic points. R_G is the position obtained from relaxing the GS. R_E is the position obtained from relaxing the ES. Point **A** is the electronic ground state, point **B** is the electronic excited state at the ground state position. Point **C** is the relaxed excited state, point **D** is the result of a vertical transition from point **C**. d_G^{FC} and d_E^{FC} are the Franck-Condon shifts. The Adiabatic Energy is used to approximate the Zero-Phonon-Line energy by neglecting the Zero-Point Energies (minimal vibrational energies in relaxed configurations)

109 **Vibrationally resolved luminescence spectra** For each electronic transition consid-
 110 ered, a vibrationally resolved spectrum is computed. The method detailed in our previous
 111 work⁵⁹ is based on the quantum harmonic oscillator model. Essentially, it consists in what
 112 is called Adiabatic Shift in the molecular community.⁷¹⁻⁷⁴ In a multi-dimensional approach

113 (nD), it considers a distinct harmonic oscillator i for every vibrational mode of the GS.
 114 All transitions from the lowest vibrational state of the excited state, $|E, 0_1, \dots, 0_n\rangle$, to any
 115 vibrationally excited ground state $|G, k_1, \dots, k_n\rangle$ ($\forall i, k_i \in \mathbb{N}$) are considered. The intensity
 116 of each of these transitions is computed in the approximation that the dipole transition
 117 moment is independent of the vibrations and positions (Franck-Condon approximation).⁷⁵
 118 As a consequence we discard the small linear dependency of the transition dipole on the
 119 displacement (the so called Hertzberg-Teller coupling). It results in a sum of contributions
 120 of the form:

$$121 \quad L(\omega) = \sum_{k_1=1}^{+\infty} \dots \sum_{k_n=1}^{+\infty} |\langle 0_1, \dots, 0_n | k_1, \dots, k_n \rangle|^2 \delta \left(\omega - E_{\text{ZPL}} + \sum_{i=1}^n k_i \hbar \omega_i \right) \quad (1)$$

122 E_{ZPL} , the Zero-Phonon-Line energy, requires the knowledge of the ES Zero-Point Energy.
 123 Unfortunately, this quantity requires the knowledge of all ES vibrational modes which is very
 124 difficult to obtain in the solid state. We instead assume that the Zero-Point energy of GS
 125 and ES are similar and thus use $E_{\text{Adiabatic}}$ to approximate E_{ZPL} . Furthermore, the overlap
 126 of ES and GS modes are computed under the approximation that ES vibrational modes are
 127 homothetic to the GS ones. This approach has already been used for the solid in some of
 128 our previous work:⁵⁹

$$129 \quad L(\omega) = \sum_{k_1, \dots, k_n} \left(\prod_{i=1}^n |\langle 0 | k_i \rangle|^2 \right) \delta \left(\omega - E_{\text{ZPL}} + \sum_{i=1}^n k_i \hbar \omega_i \right) \quad (2)$$

130 This expression can be rewritten into a more tractable form through a generative function
 131 approach, as shown in the seminal work of Kubo.⁷⁶ It implicates the computation of the mode
 132 specific Huang-Rhys factors S_i that are used in the evaluation of the $|\langle k_i | 0_i \rangle|^2$ terms. The
 133 Huang-Rhys factor for mode i is defined here by $S_i = \frac{d_{G,i}^{\text{FC}}}{\hbar \omega_i} = \frac{1}{2} \omega_i \mu_i \Delta R_i$ where μ_i is the
 134 effective mass of mode i and ΔR_i is the displacement from R_E to R_G in the direction of the
 135 eigendisplacement of mode i .⁷⁷ S_i relates to the average quantum number of the i phonon
 136 and is larger when the vibronic coupling is stronger in this direction.

137 The result of Equation 2 is a discrete spectrum made of many peaks with no width. The
138 discrete spectrum is then convoluted with a Gaussian lineshape to obtain the final spectrum.
139 To obtain the full-width-at-half-maximum of the lineshape, we use a semi-classical model of
140 the width of the total band.⁷⁸ In this model, the width of the band is obtained from the
141 dispersion of the first vibrational wavefunction of ES multiplied by the gradient of the GS
142 PES (see SI for details). This method’s applicability relies on a strong vibronic coupling, and
143 a near continuum in the GS vibrational states. As a result, it proves beneficial for analyzing
144 broad, unstructured bands.

145 It is yet impossible to evaluate the full ES PES. Consequently, more approximations are
146 required. The simplest approximation would be to assume the equivalence of ES and GS
147 PES. This would, however, systematically underestimate the dispersion because the modes
148 associated with larger displacement are likely to have significantly smaller frequencies in
149 ES than in GS. Yet, these modes are the ones contributing the most to the width of the
150 final band. As an alternative, we chose to approximate the ES PES with a single frequency
151 computed by finite difference in the direction of the GS gradient. This provides an effective
152 frequency that is most representative of the most coupled modes. This model enables a first
153 order accounting of the effect of the temperature on the band shape through the consideration
154 of a Bose-Einstein population of ES vibrational states. This temperature dependent total
155 width is used to predict a linewidth for our simulation.

156 For practical reasons, phonons required by this procedure are computed with the software
157 CRYSTAL17.^{65,79} The PBE functional is used in order to be coherent with the positions
158 obtained in previous computations.

159 To quantitatively qualify the localization of modes, we use a descriptor defined by Bell
160 and collaborators⁸⁰ named the participation ratio. The participation ratio p represents the
161 fraction of active atoms in the supercell for a given mode and is computed as follows:

$$162 \quad p_i = \frac{N_{\text{eff}}}{N} = \frac{1}{N \sum_{\alpha} \|\gamma_{i,\alpha}\|^2} \quad (3)$$

163 $\gamma_{i,\alpha}$ being the 3D vector representing the contribution of atom α to the eigenvector i .

164 An in-house (soon to be open-sourced) Python package is used to perform all the post-
165 treatments.

166 Results and discussions

167 Photoluminescence experimental spectra

168 The collected photoluminescence spectra at room temperature of samples **I**, **II** and **III** are
169 shown in Figure 2. Only sample **I** exhibits the red band that we are interested in. The blue
170 band is positioned at slightly different energies for **I**, **II** and **III**, emissions peaking at 2.98
171 eV (416 nm), 2.93 eV (423 nm) and 2.83 eV (437 nm) respectively. Simulations will explain
172 this variation (*vide infra*).

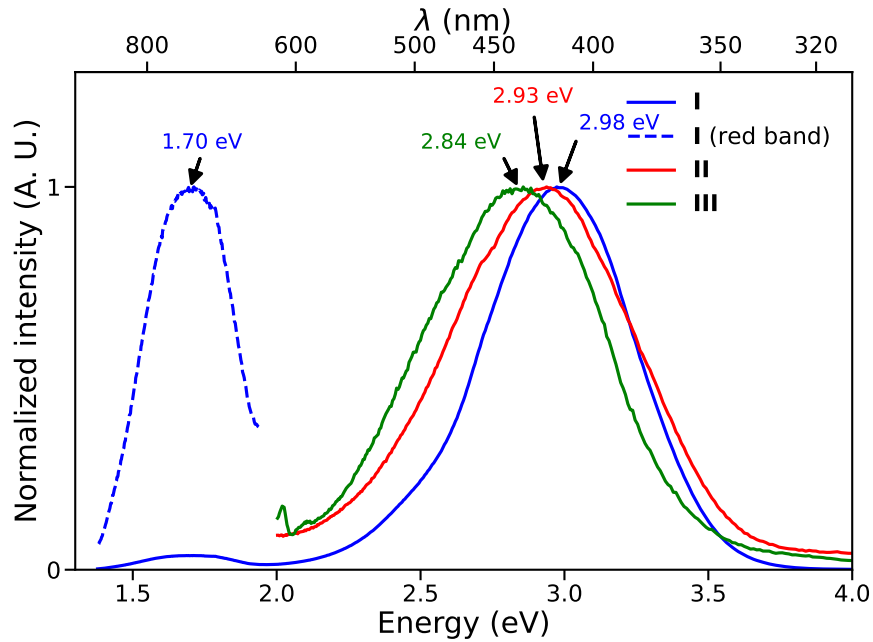


Figure 2: Recorded luminescence spectra of samples **I**, **II** and **III** at 300 K under excitation at 254 nm. The dotted line corresponds to the magnification of the blue line in the NIR-red region

173 **Computed structure and electronic structure**

174 α -Al₂O₃ crystallizes in the well-known corundum structure, where aluminum atoms are lo-
175 cated in skewed octahedra (three short and three long Al–O distances).

176 In the first coordination sphere, each AlO₆ octahedron shares a triangular face with one
177 other and three edges with three different octahedra. In the second coordination sphere,
178 each AlO₆ entity is surrounded by 6 corner shared octahedra. Oxygen atoms are located in
179 tetrahedral sites. This arrangement is illustrated in Figure 3.

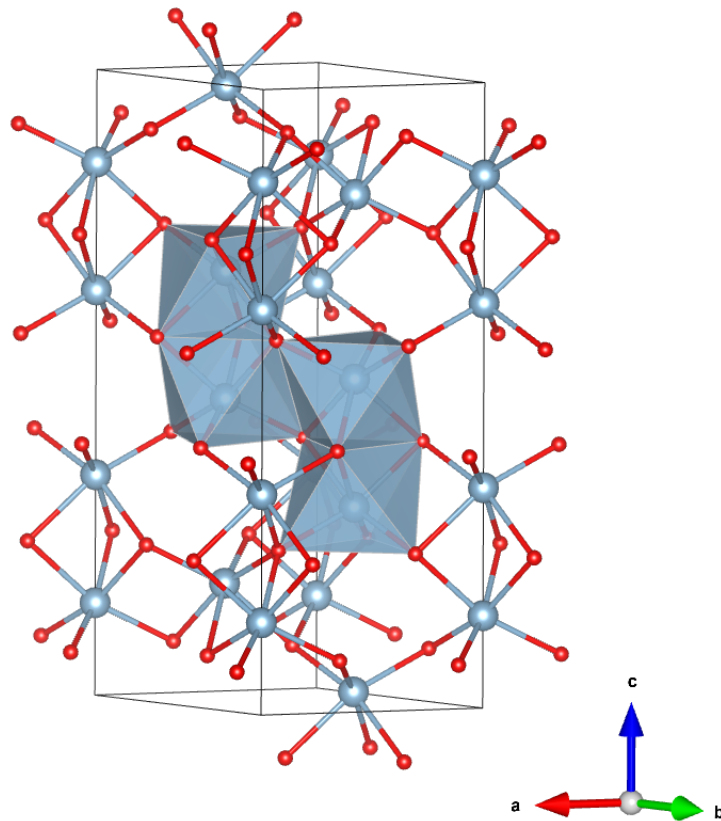


Figure 3: Conventional cell of α -Al₂O₃ with four octahedra represented to evidence the edge-sharing and face-sharing configurations. Blue and red spheres respectively represent Al and O atoms.

180 After relaxation of the pure (bulk) material, the a and c parameters are equal to 4.8063
181 and 13.1191 Å, and 4.7999 and 13.0418 Å, with the PBE (VASP) and PBE0 (CRYSTAL)
182 functionals, respectively. Both are in good agreement with experiment ($a = b = 4.7602(4)$

183 Å, $c = 12.9933(17)$ Å).⁸¹ This good reproduction of the crystalline structure is of great
 184 importance to study afterwards the possible excited states, as well as the ground state
 185 vibrational properties.

186 On these grounds (point **A** of Figure 1), the Raman spectrum of the bulk system was
 187 simulated and compared with experiment (see SI). They are in excellent agreement in terms
 188 of band position. The normal modes at 379, 430, 449, 577, and 750 cm^{-1} are of E_g symmetry
 189 whereas the modes at 418 and 645 cm^{-1} correspond to the A_g ones.

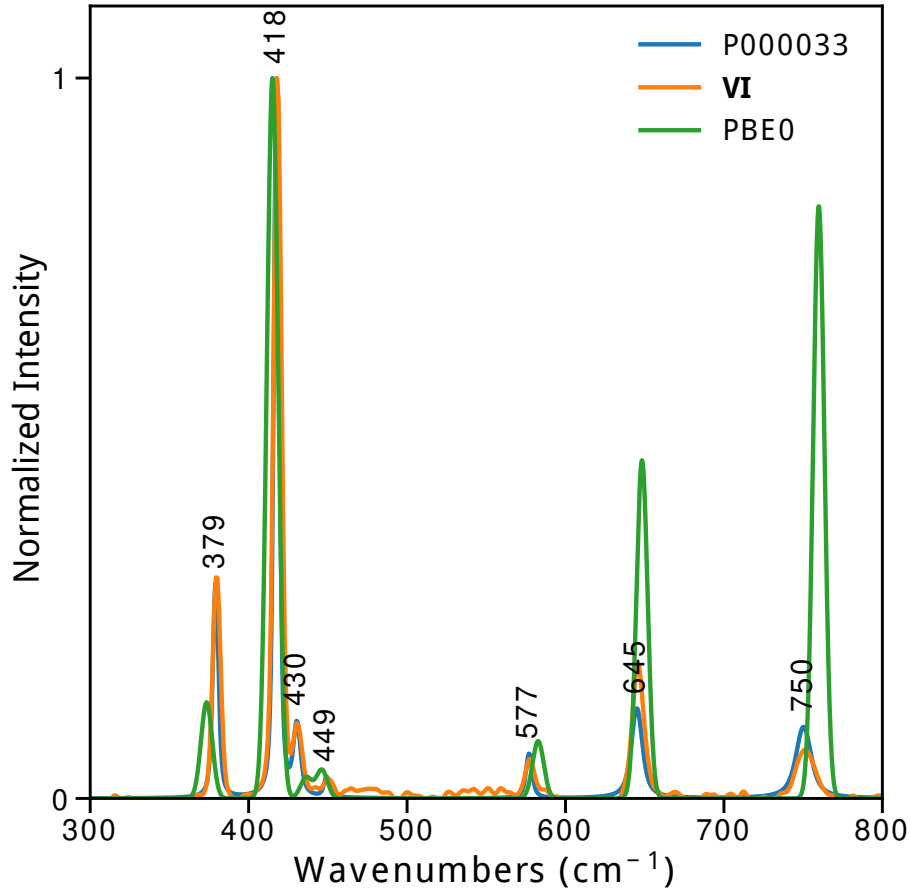


Figure 4: Experimental (P000033 sample in Ref.⁸² in blue and ultrapure compound **VI** in orange) and simulated (green) Raman spectra of sapphire using the PBE0 functional and DZVP Rev2 basis.

190 Since the geometrical parameters of the ground state and the vibrational signatures are

191 accurately modeled, it is possible to investigate confidently the properties of the faulted
192 material.

193 **Simulation of the Ti^{3+} $d-d$ transition**

194 We first consider the point defect Ti_{Al} . In such a configuration, the Ti cation has undoubt-
195 fully the +III oxidation state (formally $3d^1$). The five d levels are found inside the bulk band
196 gap. During the UV excitation process, an electron is promoted to an excited state that
197 subsequently relaxes towards an empty Ti- d orbital. The expected deexcitation process cor-
198 responds to a $d-d$ transition that triggers the red luminescence (namely $e_g \rightarrow t_{2g}$ electronic
199 transition). After relaxing the excited states, the Vertical Transition energy (E_{Vertical}) was
200 computed using the ΔSCF method. The simulated electronic emission is found around 770
201 nm (1.60 eV) which is very close to experiment (730 nm, 1.70 eV). The excellent agreement
202 between simulation and experiment allows us to accurately describe the electronic transition
203 (charge transfer). As one can see, the densities in the ground and excited states (**C** and
204 **D** points respectively in Figure 1) are localized on the titanium and can be described as a
205 combination of d orbitals (see Figure S2 in SI). Projections onto atomic orbitals show that
206 they are a combination of d_{xy} , d_{yz} and d_{zx} in the GS and a combination of $d_{x^2-y^2}$ and d_{z^2} in
207 the ES.

208 Thanks to the good reproduction of the luminescence properties, one can describe the
209 structural modifications when going from R_G (A in Figure 1) to R_E (C in Figure 1). To
210 that purpose, Ti-O distances are reported in the Table 2. As one can see, going from R_G to
211 R_E , the largest Ti-O bond lengths have increased by 11% ($\approx 0.2 \text{ \AA}$), while the smallest has
212 decreased by 3%. This is the effect of the titanium atom moving away from its face sharing
213 Al neighbor by 0.13 \AA (Ti-Al interatomic distance 4.74% longer). Such a strong geometrical
214 modification from the ground to the excited state has already been simulated in the case
215 of $\text{ZrO}_2\text{:Ti}$.⁵⁸ This is associated to the occupancy of antibonding e_g level of titanium and
216 depletion of the t_{2g} one.

Table 2: Defect–oxygen and defect–defect distances in computed structures for ground (R_G) and excited (R_E) states in the Ti_{Al} and the face-sharing $\text{Ti}_{\text{Al}}+\text{Mg}_{\text{Al}}$ defects.

	R_G	R_E
$\text{Al}_2\text{O}_3:\text{Ti}$ Ti–O (Å)	$1.98\times 3, 2.09\times 3$ (2.04)	1.92–2.32 (2.09)
$\text{Al}_2\text{O}_3:\text{Ti}$ Ti–Al [†] (Å)	2.74	2.87
$\text{Al}_2\text{O}_3:\text{Ti,Mg}$ Ti–O (Å)	$1.94\times 3, 1.99\times 3$ (1.96)	1.96–2.09 (2.03)
$\text{Al}_2\text{O}_3:\text{Ti,Mg}$ Mg–O (Å)	$1.94\times 3, 2.16\times 3$ (2.05)	$1.96\times 3, 2.13\times 3$ (2.05)
$\text{Al}_2\text{O}_3:\text{Ti,Mg}$ Ti–Mg (Å)	2.76	2.76

[†] Face sharing neighbor.

217 For each mode, the Franck-Condon shift $d_{G,i}^{\text{FC}}$ is computed by the difference of potential
 218 energy between R_G and R_E projected on the direction of the mode. The Huang-Rhys factor
 219 S_i , is a dimensionless factor that characterizes vibronic coupling, is computed as the average
 220 number of vibrational quanta in the corresponding Franck-Condon shift. The mode specific
 221 Huang-Rhys factor shown as a function of the mode energy in Figure 5 is called the phonon
 222 spectral function. In this $d-d$ transition, the defect-specific vibrational modes are found at
 223 the bottom of the energy range, in particular around 200 cm^{-1} . The mode around 200 cm^{-1}
 224 is strongly localized with a very low participation ratio ($p = 6\%$), and the main motion is
 225 the Ti^{3+} ion moving along its C_3 axis. On the other hand, higher energy modes are mostly
 226 collective motion from oxygen atoms and their contribution to the distortion is low.

227 Finally, electronic and vibrational contributions are combined into a vibronic spectrum.
 228 Figure 6 shows that it fits nicely the observed one. A band with a maximum around 1.60
 229 eV is obtained, that is only 0.1 eV lower than the experiment. This slight underestimation
 230 is to be expected from a $d-d$ transition in PBE and can be considered a very positive result.
 231 This demonstrates the strength of our computational protocol and allows us anticipating the
 232 luminescence band assignment in the blue region in the absence of fitting parameter.

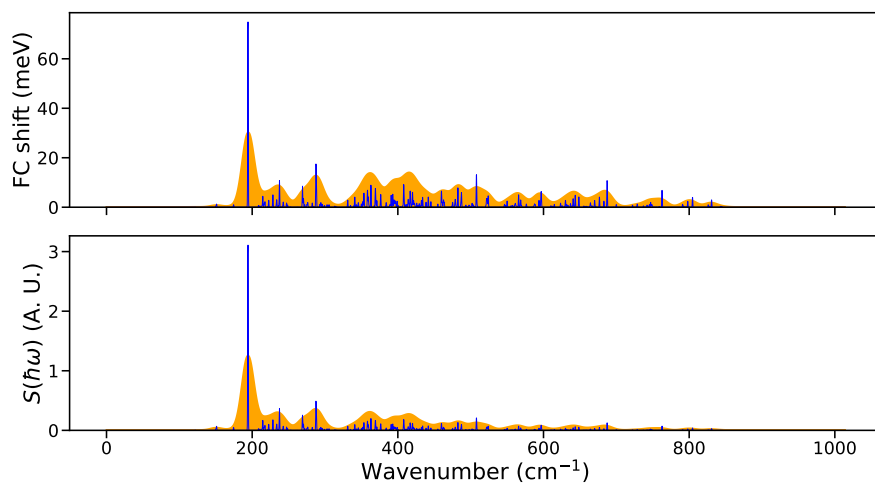


Figure 5: Phonon spectral function of the $\text{Ti}^{3+} \rightarrow \text{Ti}^{3+*}$ transition. For improved readability, an arbitrary Gaussian broadening with a standard deviation of 1 meV has been incorporated.

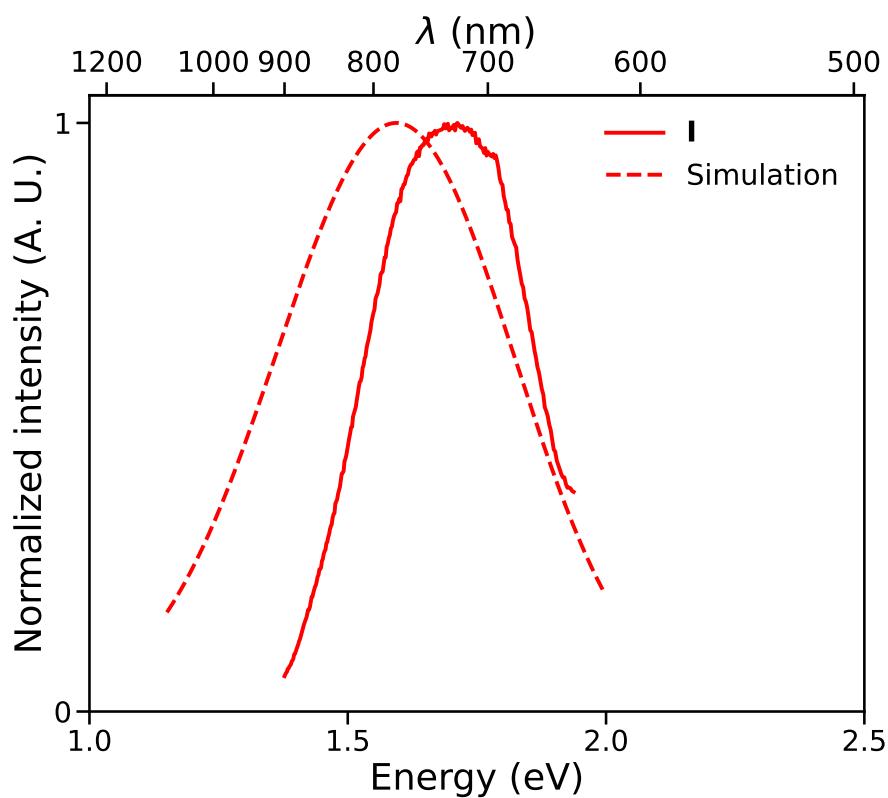


Figure 6: Experimental (solid) and simulated (dotted) luminescence spectra of the red band of **I** at 300 K. The FWHM is set to 0.6 eV.

233 Assignment of the blue luminescence

234 Based on the good agreement with experiment concerning the Ti^{3+} $d-d$ transition, we used
235 the same approach to determine the origin of the blue luminescence. Two main explanations
236 for this luminescence arise from literature: (i) the presence of oxygen vacancies (V_O^\times), and (ii)
237 a Ti–O charge transfer, involving the presence of Ti^{4+} cations at Al sites ($\text{Ti}_{\text{Al}}^\bullet$) concomitantly
238 with counteranions to balance the charge (*e.g.* X'_{Al} , X being a divalent cation).^{27–31,37–43} To
239 provide a definitive answer, we simulated both hypotheses.

240 Luminescence from an oxygen vacancy

241 For the simulation of luminescence due to oxygen vacancy, the same $2 \times 2 \times 1$ Al_2O_3 supercell
242 was considered in which one of the oxygen atoms was removed. The atomic positions were
243 then relaxed and the ground state structure (V_O^\times , neutral F center) attained. Indeed, the
244 presence of the vacancy leads to the appearance of a doubly occupied localized level inter-
245 spaced between the valence and the conduction bands. We noticed that the volume of the
246 Al_4 tetrahedron surrounding the vacancy shrunk by 6% (from 2.98 \AA^3 to 2.80 \AA^3) compared
247 to pristine Al_4O . The excited state was generated, after geometry optimization, by forcing
248 the promotion of an electron of this localized state towards the conduction band. The charge
249 density associated to this excited state (at the R_E position) is shown in Figure 7. The va-
250 cancy centered Al_4 inflated by 21% compared to the GS (from 2.80 \AA^3 to 3.38 \AA^3). The
251 charge density isosurfaces, upon deexcitation, shows the disappearance of the nodal plane
252 inside the vacancy, indicating a change of symmetry. To identify the nature of the phonons
253 involved in the distortion, we look at the phonon spectral function in Figure 8a.

254 Three main contributions arise from (i) one localized mode ($p = 14\%$) at 204 cm^{-1}
255 concerning the four Al atoms around the vacancy; (ii) one delocalized mode ($p = 42\%$) at
256 364 cm^{-1} corresponding to a bulk mode; (iii) a set of delocalized bulk modes (p from 35%
257 to 70%) from 740 cm^{-1} to 840 cm^{-1} . Finally, the simulation of the optical spectrum is
258 depicted in Figure 8b. The simulated spectrum exhibits a maximum at 445 nm (2.79 eV)

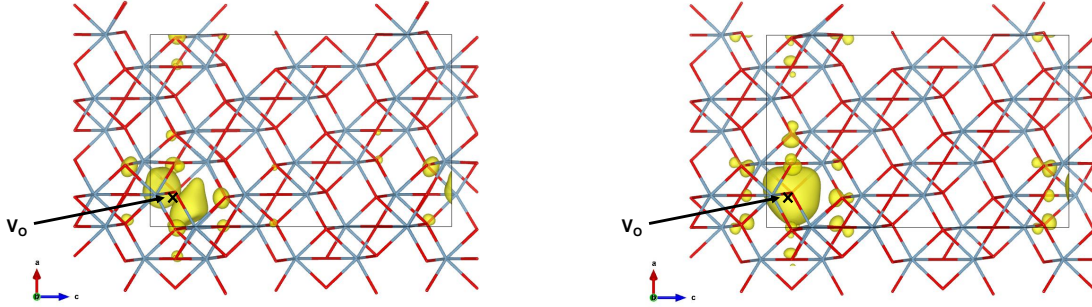


Figure 7: Charge density of frontier bands for $\text{Al}_2\text{O}_3:\text{V}_\text{O}$ in yellow. Left: excited state (**C** point in Figure 1). Right: ground state (**D** point in Figure 1). Red and cyan nodes correspond to O and Al atoms, respectively.

259 and a FWHM of 0.72 eV.

260 **Luminescence of Ti–O charge transfer**

261 As stated before, to enable a +IV oxidation state for the titanium, the substitution of a
 262 second Al by a +II codopant is mandatory. Prior to our calculations, ICP-MS measurements
 263 (Table 1) were conducted on all the samples used in this study. They confirmed the presence
 264 of various +II impurities. In all natural compounds, the ICP-MS has found the presence of
 265 Mg. Therefore, we focused our attention on this codopant. We decided to investigate three
 266 positions of the +II cation relative to the Ti(+IV); *i.e.* face-sharing (FS), edge-sharing (ES),
 267 as well as "away"; *i.e.* as far as possible in the periodic supercell.

268 The introduction of these complex defects creates new unoccupied electronic levels in the
 269 gap of the material. These levels correspond to t_{2g} and e_g states from the Ti^{4+} . The expected
 270 transition is thus a charge transfer from one Ti state in the gap to the oxygen band.

271 Nevertheless, Table 3 clearly evidences that, according to the level of theory used in
 272 the present study, it is not possible to discriminate between edge-sharing and face-sharing
 273 configurations since both simulated energies are very close to experiment. However, it is
 274 clear that the distance between the cations may be a source of variation for the transition
 275 energy. For the rest of this section, we will focus on the face-sharing case for clarity.

276 Looking at the structural distortion (Table 2) in the excited state, one can see that the

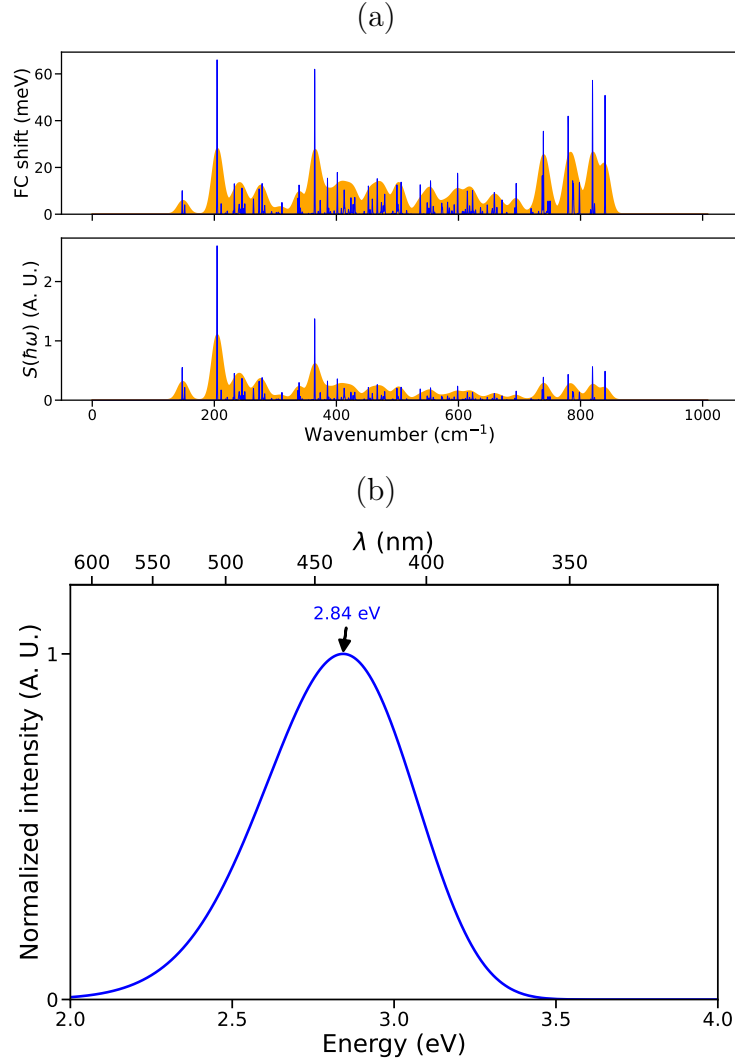


Figure 8: Phonon spectral function (a) and simulated luminescence spectrum (b) of $\text{Al}_2\text{O}_3:\text{V}_\text{O}$ at 300 K. For (a), to improve readability, an arbitrary Gaussian broadening with a standard deviation of 1 meV has been incorporated. For (b), the FWHM is set to 0.7 eV.

277 Ti–O bond lengths are the most affected ones; the longest Ti–O bond length increases by 5%
 278 (from 1.99 Å to 2.09 Å), while the Mg–O distances only slightly change (the longest distance
 279 only shrinking by 1.4%). In the face-sharing case, one can also note that the Ti–Mg distance
 280 does not vary significantly with the transition (staying at 2.76 Å).

281 We now discuss the charge transfer occurring in $\text{Al}_2\text{O}_3:\text{Ti},\text{Mg}$. The charge densities in
 282 Figure 9 clearly show a charge transfer between a Ti-*d* orbital and O-*p* close to Mg. This
 283 result follows the ones obtained by our group for several oxides.^{58,59}

Table 3: Experimental and simulated (electronic) luminescence wavelength/energy together with the computed Ti–Mg distance for the different cases dealing with the blue luminescence (Å).

		Emission (nm/eV)	Ti–Mg distance (Å)
Experiments	Trinkler <i>et al</i> (powder) ²⁹	417/2.98	—
	sample I	416/2.98	
	sample II	438/2.83	
	sample III	422/2.93	
Simulations	Al ₂ O ₃ :(Ti,Mg) (FS)	423/2.93 [†]	2.76
	Al ₂ O ₃ :(Ti,Mg) (ES)	425/2.91 [†]	2.85
	Al ₂ O ₃ :(Ti,Mg) ("away")	512/2.42 [†]	8.10

[†] Vertical transition energies

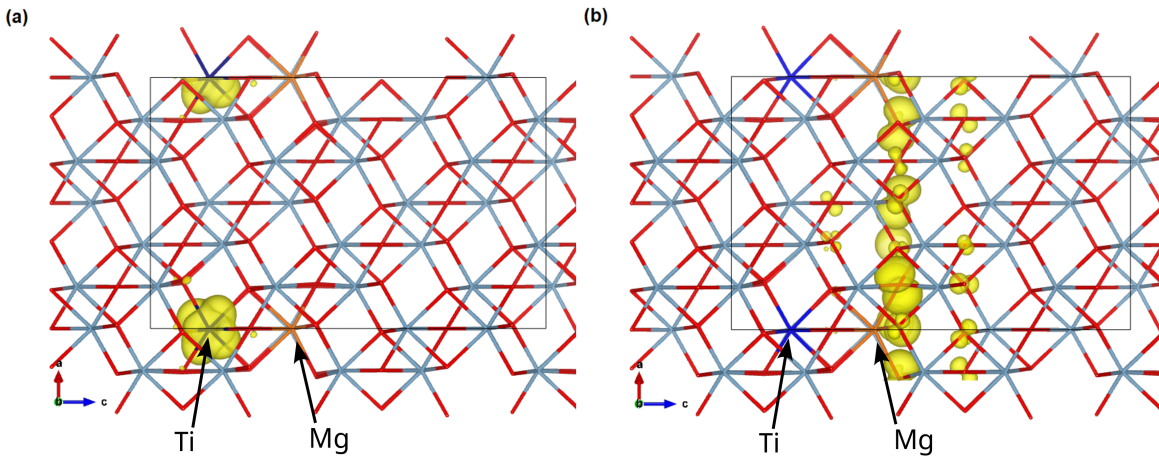


Figure 9: Charge density of frontier bands for Al₂O₃:(Ti,Mg) in yellow. Left: excited state (C point in Figure 1). Right: ground state (D point in Figure 1). Red, cyan, dark blue and orange sticks correspond to O, Al, Ti and Mg, respectively.

284 As shown by the phonon spectral function in Figure 10a the distortion is dominated by
 285 a set of delocalized ($p \geq 40\%$) modes from 750 to and 845 cm^{-1} . They correspond to bulk
 286 motions. The spectral functions for the edge-sharing case only marginally differ from the
 287 aforementioned one (see SI). In the "away" case, the same overall structure is found, with
 288 a more contrasted contribution of the higher energy modes and a larger total Huang-Rhys
 289 factor ($S_{\text{total}} = \sum_i S_i$).

290 Finally, the simulation of the luminescence spectrum of the Al₂O₃:Ti,Mg, showed in

291 Figure 10b produces bands that are centered around 3.02 eV, 2.98 eV and 2.60 eV for face-
292 sharing, edge-sharing and away cases respectively.

293 **Discussion**

294 The simulations show a band around 2.87 eV for V_O and bands 3.02 eV, 2.98 eV and 2.60 eV
295 for Ti,Mg FS, ES and "away", respectively. To identify the contribution of each transition in
296 the observed luminescence bands, fits of a weighted sum of different theoretical transitions
297 are performed. Moreover, the FS and ES transitions are too close to be distinguished.
298 Consequently, the ES contribution is excluded in the summation leaving Ti,Mg FS, Ti,Mg
299 "away" and V_O transitions for the band assignment. In all the fits, the same individual bands
300 are used with only a weight prefactor. The result of these optimizations are displayed in
301 Figure 11. Interestingly, it shows that the sample **I** exhibits mostly Ti,Mg FS luminescence,
302 with a small contribution of V_O . It is to be noticed that **I** show that the width predicted
303 in this approach is probably slightly overestimated, preventing as good a fit as for the other
304 samples. The sample **II** sample shows similar results, with a small added contribution of
305 the Ti,Mg away spectrum. Finally, the luminescence of sample **III** can mostly be explained
306 by vacancies, with a small contribution of Ti,Mg away. As one can see, in the absence of
307 any fitting parameters except for the relative importance of each transition, the simulated
308 spectra fit nicely experiment.

309 **Towards a predictive model**

310 On these grounds, the predictive capability of our methodology was tested. To do so, only
311 the luminescence spectra of Ti,Ca FS and Ti,Be FS were simulated in a similar way to Mg.
312 For long Ti–M distances, no effect of the nature of the codoping cation is expected on the
313 luminescence as only the long-distance coulombic interaction remains. As a consequence, for
314 the new cations, only the FS configurations have been considered. The Ti,Ca model predicts
315 a large band centered around 2.70 eV (FWHM = 0.84 eV) while the Ti,Be one yields a

316 similarly large band centered around 3.24 eV (FWHM = 0.75 eV). The photoluminescence
317 of the beryllium-diffused material (sample **V**) together with the syntheses of Al₂O₃ codoped
318 with Ti,Ca (sample **IV**) were recorded. Since the ICP-MS (Table 1) shows the presence
319 of Mg and Ca in both samples, the decompositions of both spectra included the simulated
320 Ti,Mg (FS) and Ti,Ca (FS) spectra.

321 The Ti,Be spectrum was also used in the decomposition of the sample **V**. The results of
322 these decompositions are shown in Figure 12.

323 The sample **V** shows no contribution of the Be related band. Instead, we find a contri-
324 bution of the vacancies that can be compared with the other natural sample (**II**) as well as
325 significant contributions of Mg and Ca related bands, as expected from the ICP-MS.

326 The sample **IV** shows a large contribution of vacancies, like the other powder (**III**), as
327 well as a significant contribution of the Ca band. The Ti,Mg band is also present.

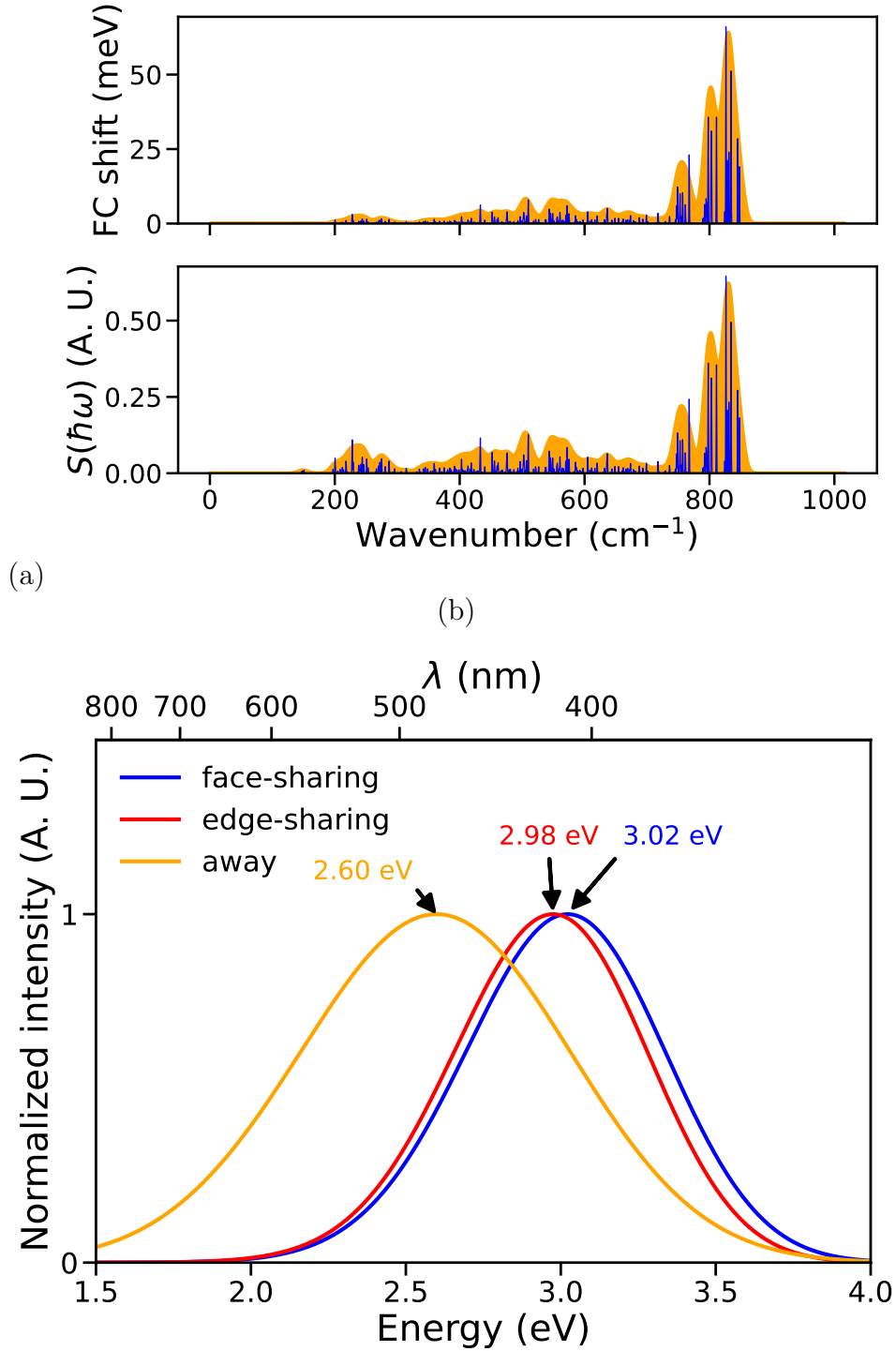


Figure 10: Phonon spectral function (a) for the FS Ti,Mg transition and (b) comparison of the three cases of Ti,Mg spectra simulations at 300 K. The band FWHM are 0.66 eV, 0.66 eV, and 0.82 eV respectively. For (a), to improve readability, an arbitrary Gaussian broadening with a standard deviation of 1 meV has been incorporated. For (b), the FWHM were set 0.66, 0.66 and 0.82 eV for the curves in blue, red and orange, respectively.

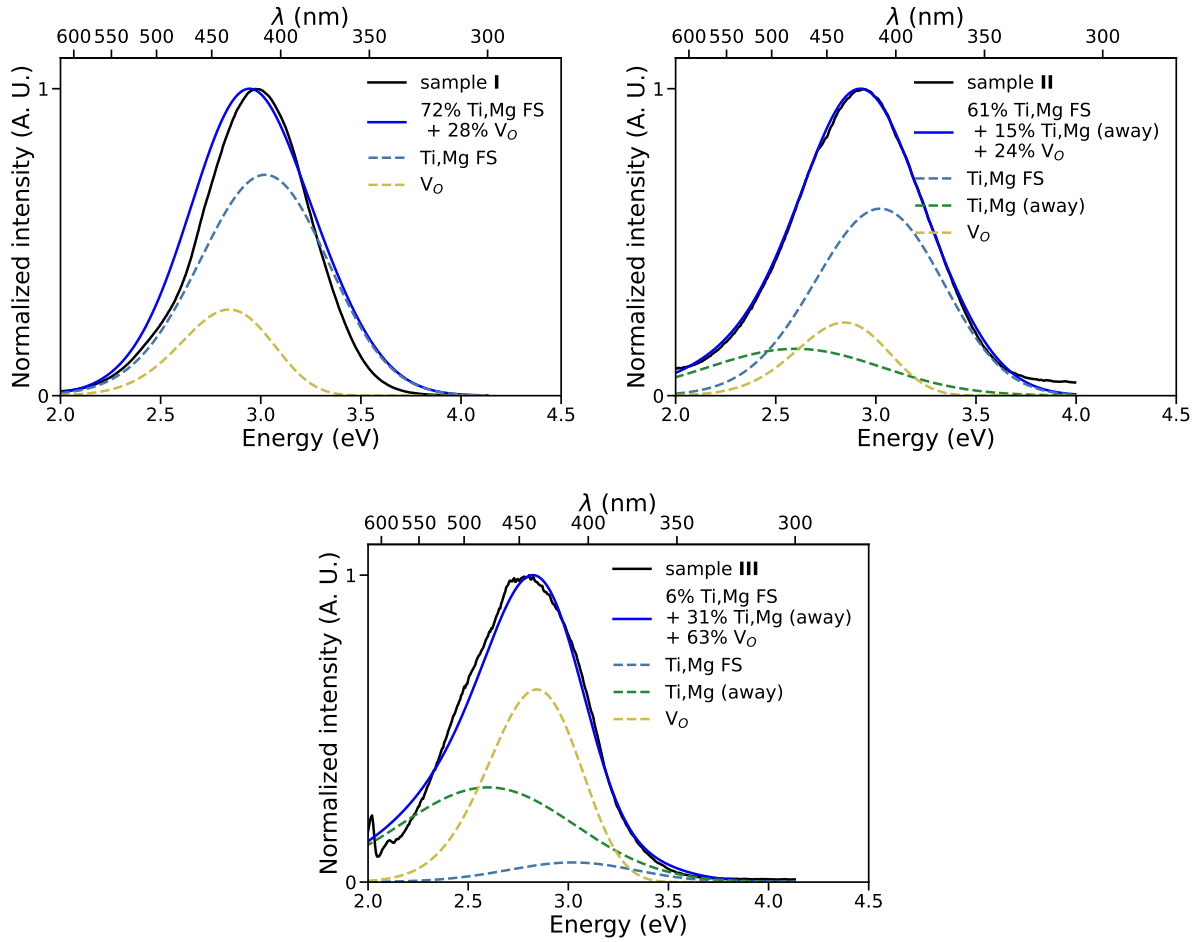


Figure 11: Results of fitting the experimental spectra with a combination of V_O and Ti,Mg spectra.

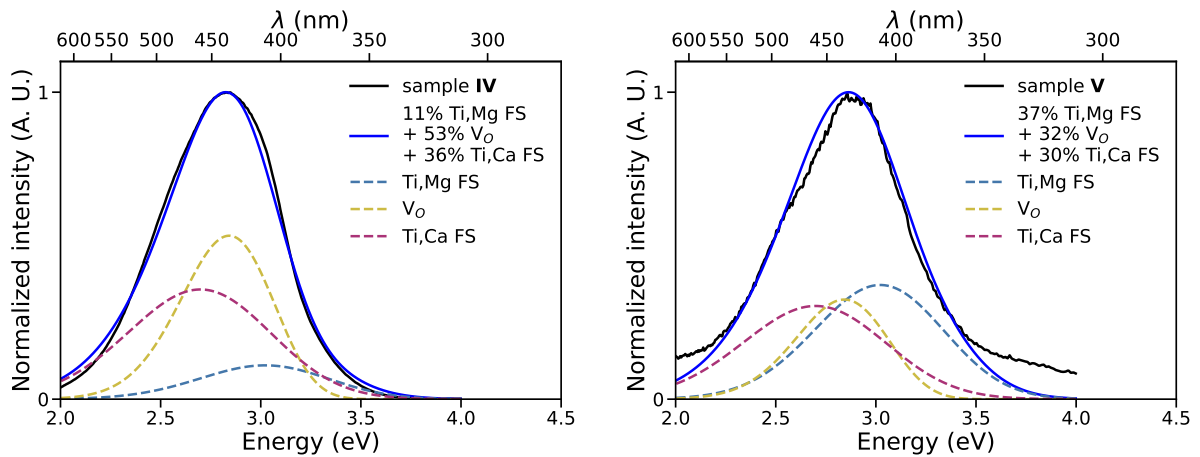


Figure 12: Decomposition of the luminescence of samples IV and V into the simulated spectra.

328 **CIE(x, y) diagrams**

329 We would now be able to simulate the color of the samples luminescence. We used all the
330 fitted compositions and the corresponding samples and computed chromaticity coordinates
331 from the spectra. For the sample **I**, we also added the red band associated with Ti^{3+} to the
332 composition of the spectrum. As absolute intensities are not yet available in our simulation
333 protocol, we used the relative intensity between the two experimental bands of 1:27 to
334 combine the simulated bands.

335 The results are provided in a CIE chromaticity diagram in Figure 13. Coordinates of all
336 the points are detailed in SI. As one can see the reproduction of colors is very accurate.

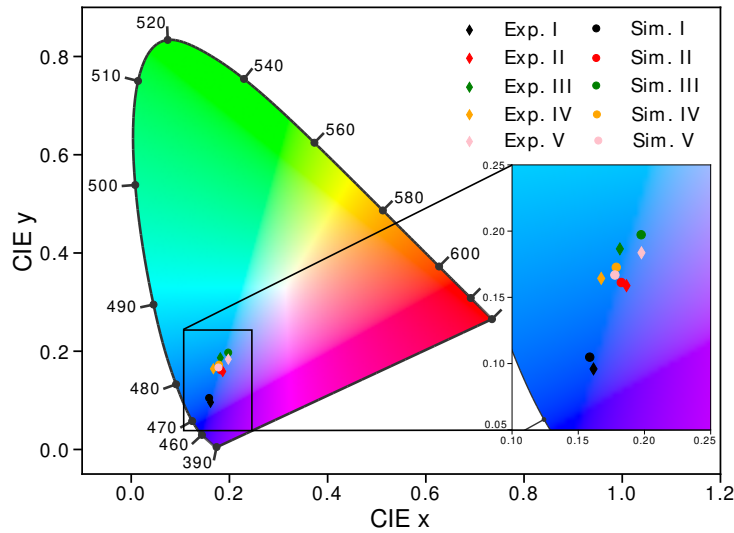


Figure 13: CIE chromaticity diagram for all samples and their associated simulations.

337 **Conclusion**

338 In this paper, we demonstrated that we are able to accurately simulate the luminescence
339 spectra of $Al_2O_3:Ti$ for various compositions. First, we were able to reproduce the well-
340 known red luminescence of the Ti^{3+} *d-d* transition and the charge density confirms our
341 capability to deal with *d¹* transition.

342 Second, we were able to show that the blue luminescence results from several processes
343 including both the oxygen vacancies and the possible presence of a Ti,M codoping. Our
344 model unambiguously reproduces the blue band with a high accuracy.

345 Finally, the simulated CIE chromaticity diagrams agree with the experiment.

346 These results based on parameter-free method open new possibilities for experimentally
347 and theoretically oriented chemists to interact, since we can now successfully simulate excited
348 state properties.

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356 **Supporting Information Available**

- 357 • Details of atomic distances in $\text{Al}_2\text{O}_3\text{:Ti}$ and $\text{Al}_2\text{O}_3\text{:Ti,Mg}$;
- 358 • Charge density representation of frontier bands in $\text{Al}_2\text{O}_3\text{:Ti}$ in ground an excited state;
- 359 • Projected density of state of ground state $\text{Al}_2\text{O}_3\text{:Ti,Be}$, $\text{Al}_2\text{O}_3\text{:Ti,Mg}$, and $\text{Al}_2\text{O}_3\text{:Ti,Ca}$;
- 360 • XRD patterns of synthesized samples **III** and **IV**;
- 361 • Bandwidth approximation from ES PES;
- 362 • Synthesis protocol;
- 363 • Experimental and Simulated CIE coordinates

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