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1 THIRD ORDER NON-LINEAR OPTICAL SUSCEPTIBILITIES ($\chi^{(3)}$) OF YTTRIA STABILIZED
2 CUBIC HAFNIUM(IV) OXIDE

3 HASSAN DENAWI¹, JACQUES K. DEMARAI^{1,2}, C.S. PRAVEEN³, MICHEL RERAT¹ AND
4 PANAGHIOTIS KARAMANIS^{1*}

5 ¹*E2S UPPA, CNRS, IPREM, Université de Pau et des Pays de l'Adour, 64053 Pau, France*

6 ²*International School of Photonics (ISP), Cochin University of Science and Technology
7 (CUSAT), Kalamassery, Ernakulam, Cochin, Kerala, 682022, India*

8 ³*Dipartimento di Chimica, Università di Torino, via Giuria 5, 10125 Torino, Italy blications Department*

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**panagiotis.karamanis@gmail.com*

11 **Abstract:** This work reports for the first time theoretical third order nonlinear optical susceptibilities of
12 YSH bulk phases which are key properties for telecommunication technologies and integrated photonic
13 devices. Our outcomes, relying on coupled perturbed Kohn-Sham density functional theory expose that
14 the NLO capacity of YSH should be similar to another material of this family, namely, yttria stabilized
15 zirconia that has been proposed as a promising candidate for integrated photonics by Marcaud et al
16 [Photon. Res. **8**, 110 (2020)]. Finally, evidence implying important vibrational contributions to the
17 optical nonlinearities of the systems are revealed and analyzed.

18

19 **1. Introduction**

20 The key to harness light's nonlinear effects and to unlock its "limitless" potential in
21 telecommunication technologies lies in the successful and cost-effective fabrication of fully
22 operating integrated nonlinear photonic devices. [1,2] Upon success, ultra-fast optical
23 processing at femtosecond time scales, having the capacity to give access to petahertz
24 telecommunication bandwidths, could eventually be achieved. In this realm, one of the main
25 properties of interest is the so called intrinsic third order non-linear optical (NLO) susceptibility,
26 3] routinely designated as $\chi^{(3)}$. The latter band-gap dependent property provides the means to
27 control light with light, [4] via the so-called Kerr effect which reflects the ability of a given
28 material to change its refractive index upon the application of an electric field. In this context,
29 Marcaud *et al.* [5] reported the outcomes of a joint experimental and theoretical work dealing
30 with the NLO behavior of yttria stabilized zirconia (YSZ). As demonstrated in that work, YSZ,
31 that can be grown epitaxially [6] on silicon substrates, features a comparable third order

32 nonlinear effective Kerr coefficient (\hat{n}_2) with silicon nitride.[7] The latter material although it
33 is one of the materials of choice for integrated photonics it suffers from significant
34 shortcomings due to strong two photon absorption (TPA) effects that induce significant optical
35 losses (see ref [5] and references therein). As Marcaud *et al.* concluded, TPA losses in YSZ are
36 expected to be negligible thanks to its large bandgap and its quasi-cubic local atomistic
37 structure. [5]

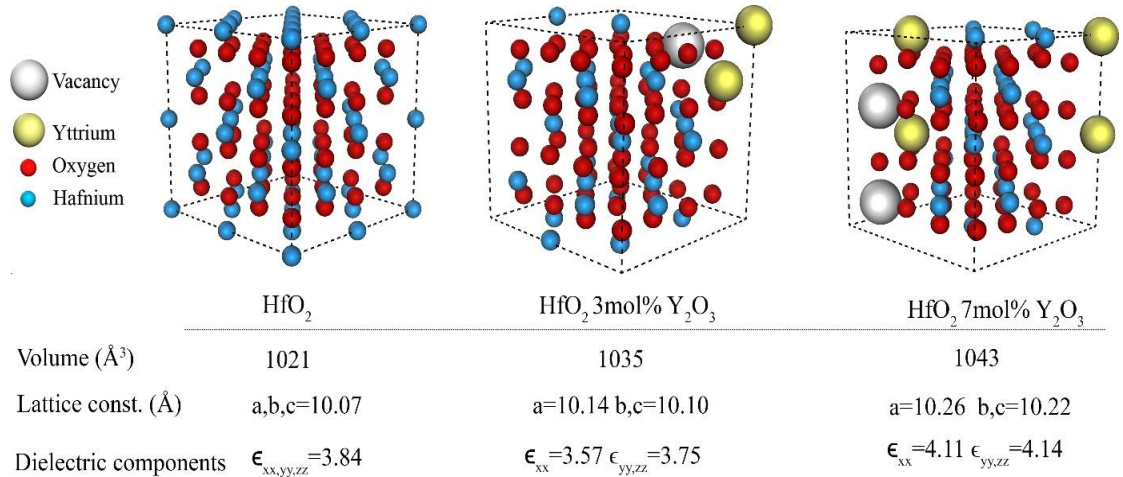
38 Motivated by the intense technological interest in the optical properties of functional oxides
39 for integrated photonic devices worldwide, in this article, we report on reliable $\chi^{(3)}$ estimations
40 of another widely recognized functional oxide, namely, yttria stabilized hafnia (YSH). Hafnia
41 (HfO_2),[8] the parent material of YSH, is known to possess four crystalline phases[9], namely,
42 tetragonal, monoclinic, cubic and amorphous. Out of the four hafnia phases the third one (c-
43 HfO_2) is of great interest in CMOS technologies owed to its high dielectric constant and wider
44 band gap. [10] However, cubic hafnia becomes “functional” only in quite high temperatures
45 (> 2500 °C)[11] and this impedes its application in many areas including optoelectronics.
46 Therefore, its stabilization at ambient conditions via doping is one of the preferred options. For
47 this task, Y_2O_3 has proven a highly effective doping agent since it “stabilizes” hafnia’s cubic
48 phase even in relatively low concentrations ranging from 0.6 mol% to 6.5 mol%. In particular,
49 the current work reports on accurate coupled perturbed electronic static $\chi_{iii,ijj}^{(3)}$ macroscopic
50 data defined as:

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$$\chi_{iii,ijj}^{(3)} = 2\pi\gamma_{iii,ijj}^e(3V)^{-1}$$
 (where, i and j are the cartesian cell axes)

52 In Eq. (1) γ^e is electronic contribution of the second hyperpolarizability per unit cell volume
53 (V). The latter quantity can be determined experimentally⁷ via measurements of the refractive

54 index: $\hat{n}_2 = 3\hat{\chi}^{(3)} (4c\epsilon_0\epsilon)^{-1}$ (ϵ is the relative dielectric in-plane ϵ_{xx} component, ϵ_0 the
 55 electric permittivity of vacuum and c the light velocity and $\hat{\chi}^{(3)}$ is the effective third order
 56 susceptibility[5]).

57 **2. Results and discussion**
 58



59 **Fig. 1.** Relaxed stoichiometric atomistic super-cells YSH. All structures are true minima of the corresponding
 60 supercell potential energy super-surfaces.
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62 All computations presented and discussed here have been carried out using widely tested
 63 density functional methods (DFT) as implemented in CRYSTAL17 code. [11] In brief, the
 64 generalized gradient approximation (GGA) functional of Perdew, Burke, and Ernzerhof (PBE)
 65 and the hybrid functionals PBE0 and B3LYP, have been employed to check the method
 66 dependence on the properties of interest. A supercell size of $2 \times 2 \times 2$ has been considered for
 67 the disordered and vacancy calculations with a corresponding Monkhorst-Pack grid [12] of $8 \times$
 68 8×8 . The spatial doping/vacancy distribution chosen has been based on earlier benchmark
 69 computations initially carried out on YSZ [5] and applied here on YSH. Although our structural
 70 investigation is not exhaustive, our experience on YSZ [5] phases suggests that there is a minor
 71 influence of the local atomistic structures of such oxides on the electronic part of their third

72 order nonlinearities which is expected to dominate the overall response. The computation of
 73 the linear and nonlinear properties addressed here relied on coupled perturbed Kohn-Sham
 74 density functional theory as implemented [13] in CRYSTAL 17 by one of the authors of this
 75 study. For Y and Hf atoms, we relied on pseudo-potential (ECP) basis set constructed by Hay-
 76 Wadt and Stevens *et al.*, respectively [14,15] For O atoms, the Durand-Barthelat[16] ECP basis
 77 set was chosen in which the $1s^2$ core electrons are approximated by a nonrelativistic potential.

78 Table 1. Energy Band Gaps (Eg, in eV) of HfO₂, YSH and YSZ, obtained within a plane wave and
 79 crystalline orbital calculations.

	PBE	PBE0	B3LYP
c-HfO ₂	4.04	6.47	6.03
3.2%YSH	4.38	6.77	6.26
6.7%YSH	4.56	6.98	6.45
6.7%YSZ	3.58	5.83	5.39

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82 The relaxed stoichiometric atomistic super-cell structure of c-HfO₂ (2×2×2) as well as two
 83 cells of YSH of the same size containing 3.2 and 6.7 mol% of Y₂O₃, (hereafter (3.2%,6.7%)
 84 YSH), considered in this report are illustrated in **Fig. 1**. Our structural results for c-HfO₂, also
 85 shown in the latter figure, are in good agreement with previously theoretical and experimental
 86 outcomes reported by Zhao and Vanderbilt [17] within the local density and generalized
 87 gradient approximation and close to the experimental value [18] of 5.08 Å per unit cell (10.16
 88 Å for a 2×2×2 supercell). According to our knowledge up until now, no experimental or
 89 theoretical structural data have been reported for either concentration of YSH.

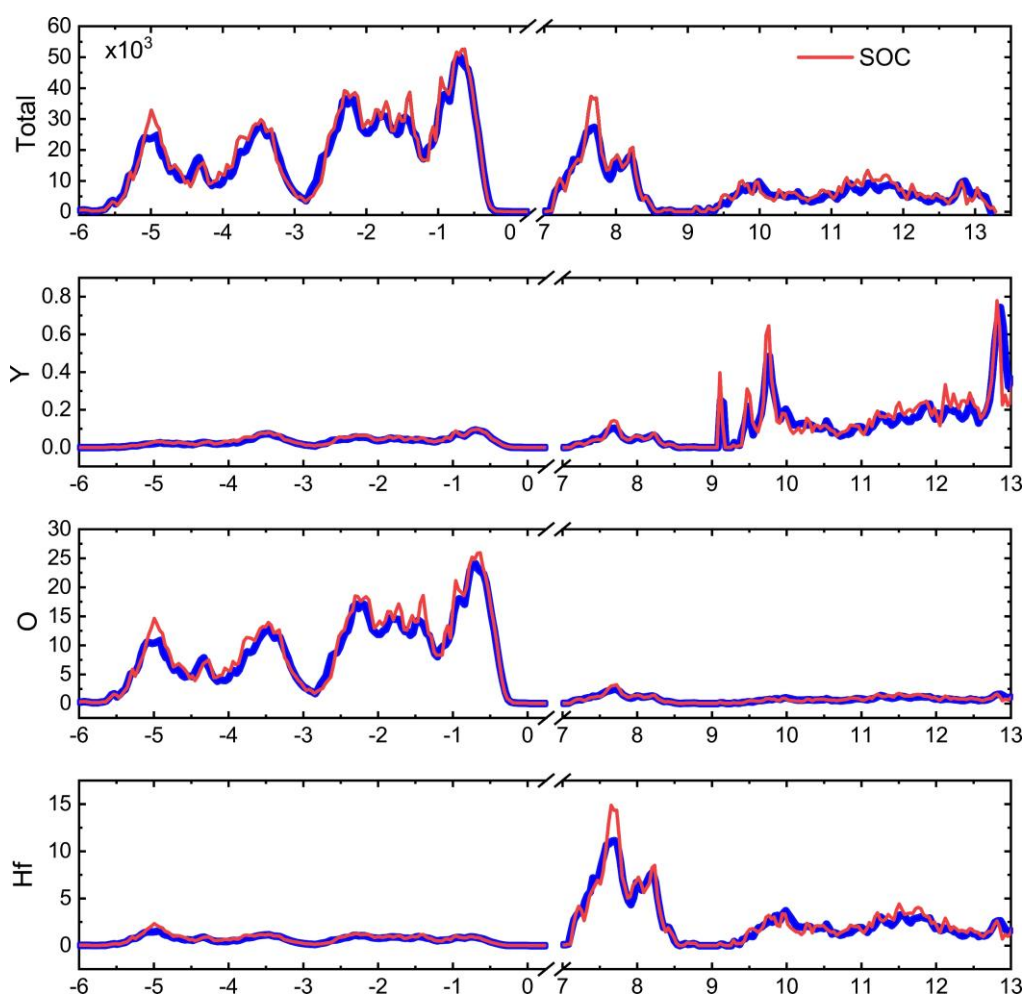
90 The energy bandgap values of the above compositions, computed with a pure DFT
 91 functional (PBE), and two different hybrid functionals (PBE0, B3LYP), are presented in **Table**

92 1. As expected, PBE functional, the least expensive computational method used here in, delivers
93 considerably smaller bandgaps with respect to the two hybrids PBE0 and B3LYP. A direct
94 comparison of our computed band gap of c-HfO₂ with spectroscopic ellipsometry
95 measurements of 5.8 eV reported by C. Adelman *et al.* [19] reveals that the two hybrids, PBE0
96 and B3LYP, predict considerably improved bandgap energies lying about 0.7 and 0.2 eV above
97 the experiment, respectively. We expect similar method behavior for YSH phases considered
98 in this work.

99 As far as it concerns the dependence of YSH bandgap on the doping concentration,
100 our computational outcomes, clearly suggest that doping c-HfO₂ with yttrium induces a
101 noticeable bandgap broadening. The observed evolution is in accord with the trend reported
102 by Chen *et al* [20] who studied the dependence of Y₂O₃ concentration on the optical properties
103 of crystalline HfO₂ thin films via spectroscopic ellipsometry and concluded to a proportional
104 dependence of the measured band gaps with respect to the doping concentration. Spin-orbit-
105 coupling effects (SOC) on the band structures of pure and doped hafnia using richer basis sets
106 [21, 22, 23, 24]. for all atoms have been considered by applying a newly developed scheme in
107 CRYSTAL based on two-component spin-current density functional theory [25,26]. In brief, For Y
108 and Hf we used a fully relativistic effective core potential (ECP) including both the scalar-
109 relativistic AREP and the spin-orbit SOREP parts, developed by Peterson *et al.* [27] and
110 Figgen *et al.*[28]. For Y, an associated valence basis set of triple-zeta quality was available for
111 solid-state calculations reported by Laun *et al.*[29] In the case of Hf, the basis set applied was
112 derived from the associated correlation-consistent double-zeta set for molecular calculations
113 provided by Peterson *et al.*[24] after we uncontracted the set and removed Gaussians with
114 exponents smaller than 0.1 a.u to avoid linear dependencies. Our final uncontracted Hf valence

115 basis set is available at CRYSTAL basis set library [30] For O we used the basis set from
116 Heifets et al. [31]

117 The computations, carried out on the optimized supercells of **Fig. 1**, exposed that SOC brings
118 minor corrections on the band gaps of all systems considered. Specifically, for pure c-HfO₂
119 SOC increases the respective band gap by 0.004 eV while in the case of 3.2% and 6.7% YSH
120 a bandgap opening by 0.007 and 0.006 eV is delivered, respectively. Furthermore, as it can be
121 easily seen in **Fig. 2**, where we depict the total (DOS) and projected (PDOS) density of states
122 of 3.2% YSH, the weak spin-orbit-coupling effects evidenced in the band splitting is transferred
123 also on the shape and intensity of the computed DOS and PDOS spectra.



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Fig. 2. Total and projected densities of states for 3.2% YSH obtained at the PBE0. Red colored (P)DOSS spectra correspond to computations considering spin-orbit-couplings (SOC).

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Table 2. Electronic contribution to the dielectric $\epsilon_{xx}, \epsilon_{yy=zz}$ components, to the third order susceptibilities $\chi_{xxxx}^{(3)}, \chi_{yyyy=zzzz}^{(3)}, \chi_{yyzz}^{(3)}$ components ($\times 10^{-21} m^2 V^{-2}$), of HfO₂, YSH 3.2% and 6.7% mol.in Y₂O₃ and YSZ 6.7% mol. in Y₂O₃. In this case x, y and z are placed parallel to the lattice constants a, b and c , respectively.

		$\epsilon_{xx} = \epsilon_{yy} = \epsilon_{zz}$	$\chi_{xxxx}^{(3)} = \chi_{yyyy}^{(3)} = \chi_{zzzz}^{(3)}$			$\chi_{yyzz}^{(3)}$
c-HfO ₂	PBE0	3.8	0.9			0.7
	B3LYP	3.9	1.1			0.8
		$\epsilon_{xx} = \epsilon_{yy}$	ϵ_{zz}	$\chi_{xxxx}^{(3)}$	$\chi_{yyyy}^{(3)} = \chi_{zzzz}^{(3)}$	$\chi_{yyzz}^{(3)}$
3.2% YSH	PBE0	3.6	3.7	0.7	0.8	0.6
	B3LYP	3.7	3.8	0.9	0.9	0.7
6.7% YSH	PBE0	3.5	3.7	0.6	0.7	0.6
	B3LYP	3.6	3.8	0.8	0.9	0.6
6.7% YSZ	PBE0	4.1	4.14	1.2	1.2	1.0
	B3LYP	4.2	4.25	1.5	1.4	1.2

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Let us now turn our attention to **Table 2** that summarizes our analytical CPKS outcomes of the dielectric components and the electronic part of the third order NLO susceptibilities of undoped hafnia, 3.2%, 6.7% YSH and 6.7% YSZ. Starting from the relative dielectric tensorial components we see that yttrium doping delivers a slight anisotropy with respect to the perfect cubic phase. This trend is also followed by the computed third-order susceptibilities. Moving now to the properties of interest we see that for all systems both functionals yield third-order susceptibilities not far from the limit of $10^{-21} m^2 V^{-2}$ which is considered adequate for certain photonic applications [5]. In addition, it becomes evident that yttrium doping delivers a slight decrease in $\chi_{yyyy}^{(3)}, \chi_{zzzz}^{(3)}$ and $\chi_{yyzz}^{(3)}$ components, a result that is in accord with the evident

151 bandgap widening occurring upon Y doping due to the inverse proportionality of $\chi^{(3)}$ to the
152 bandgap of a given material. If we now directly compare the third order nonlinearities of
153 6.7% YSH to its zirconia analogue, that in this case shares the same local atomistic structure, it
154 is revealed that both lattices feature $\chi^{(3)}$ values of a similar order of magnitudes with the latter
155 being about two times more hyperpolarizable than the former. The revealed ordering is in
156 accord with the wider band gap values of YSH. Furthermore, to facilitate the comparison with
157 previous, and more importantly, future experimental measurements for similar systems, we
158 have used the tensorial components shown in **Table 2** to calculate the effective Kerr coefficient
159 \hat{n}_2 of and as shown by Marcaud *et al.*[5] The obtained outcome of $0.8 \times 10^{-19} \text{m}^2 \text{W}^{-1}$ for 6.7% YSH
160 at B3LYP level, lies about 1.6 times lower than the effective Kerr coefficient of 6.7% YSZ
161 obtained at the same level of theory.

162 Bearing in mind that the nonlinearities discussed so far correspond to the electronic part of
163 $\chi^{(3)}$, one should regard the nonlinear coefficients listed in **Table 2** as the lowest limit at each
164 level of theory. Based on previous results for YSZ, we expect that the actual NLO response of
165 YSH should be even stronger owed to a combination of effects related to the frequencies of the
166 applied dynamic or oscillating electric fields (c.c. frequency dispersion), possible thermal
167 lattice expansions, and more importantly to vibrational contributions.[32] To address the latter
168 effects we relied on the variation of the dipole polarizability of each unit cell with respect to
169 the atomic displacement along the axial supercell directions. For this task, we applied the
170 formulation corresponding to one of the most common NLO processes, namely, the intensity-
171 dependent refractive index (IDRI). In this process and by means of the so-called infinite-
172 frequency approximation, [33] the harmonic diagonal vibronic contribution is simplified as:

173
$$\gamma_{xxxx,yyyy,zzzz}^{vib} \simeq 2 \sum_{k=1}^{3N-3} \frac{\left(\frac{\partial \alpha_{xx,yy,zz}^e}{\partial Q_k} \right)^2}{\omega_k^2} \quad (2)$$

174 In Eq. (2) N is the number of atomic centers comprised in the unit cell and $\frac{\partial \alpha_{xx,yy,zz}^e}{\partial Q_k}$ the
 175 derivative of the axial dipole polarizability component per unit cell with respect to the harmonic
 176 normal Q_k -mode with ω_k -frequency. The obtained analytical outcomes within the CPKS
 177 approximation are presented in **Table 3** and reveal that for pristine hafnia the vibrational
 178 contributions are extremely weak with respect to the electronic ones. In striking contrast, our
 179 computations at the PBE0 level expose a strong vibrational contribution of 3.0×10^5 and 3.2×10^5
 180 a.u. along the x -axis of the unit cells of 3.2% YSH and 6.7% YSH, respectively. As a result, a
 181 γ_{xxxx}^{tot} value of 9.5×10^5 a.u. which lies about 1.5 times higher than the corresponding γ_{xxxx}^e value
 182 of 3.2% YSH, has been obtained. A similar behavior is observed for 6.7% YSH.

183 Taking into consideration that the computed RAMAN intensities are proportional to the
 184 square of the first derivative of the dipole polarizability with respect to the corresponding
 185 displacement mode, the revealed vibrational effects can be rationalized up to a great extent by
 186 a careful analysis of the simulated RAMAN spectra shown in **Figure 3**. Thereby, we see that
 187 the spectrum of pure cubic hafnia is characterized by a single strong absorption band at 640 cm^{-1}
 188 ¹. Despite its large intensity, the respective absorption band lies too high in energy to induce
 189 strong vibrational contributions to the second dipole hyperpolarizability along any Cartesian
 190 cell direction. On the other hand, in the RAMAN spectra of the two YSH phases one can easily
 191 spot several soft active absorption bands appearing in low energies. Their origin should be
 192 attributed to the weak but evident deviation from the cubic symmetry of the doped YSH
 193 supercell due to the replacement of two

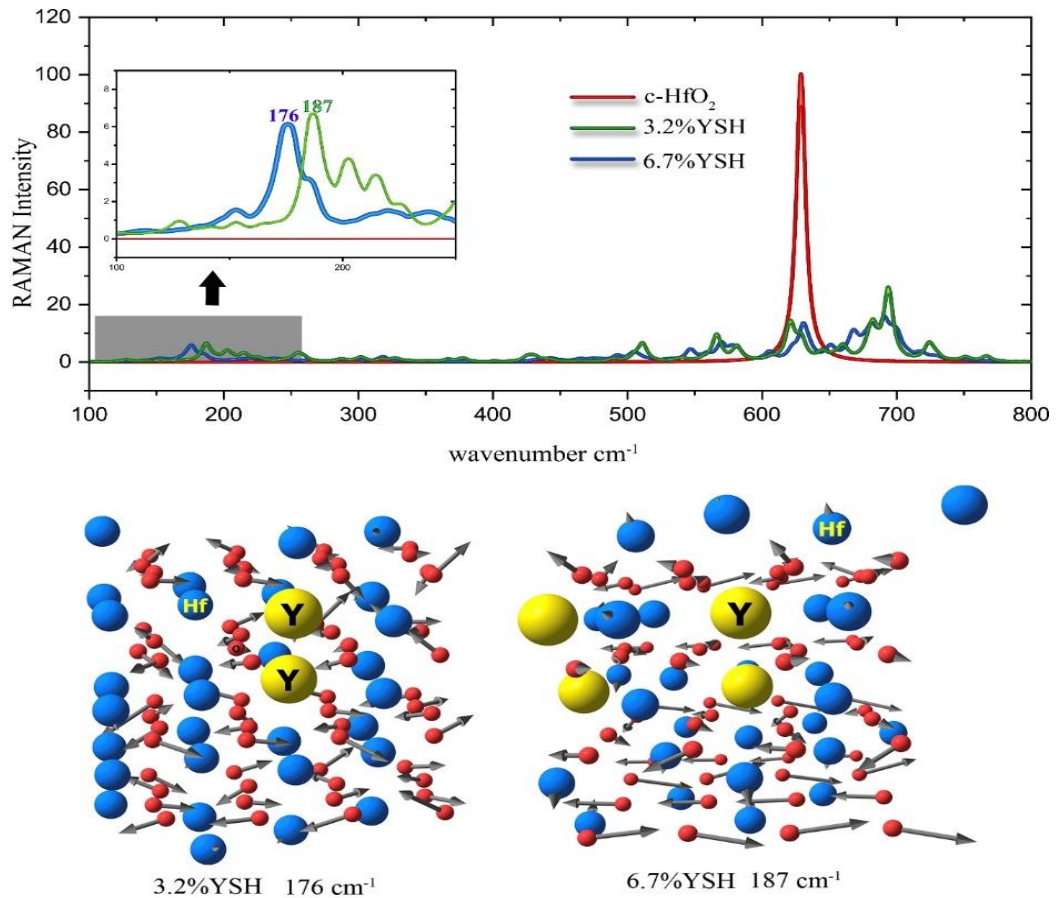
194 Table 3. Unit cell electronic (γ^e), vibrational (γ^{vib}), and total ($\gamma^{tot} = \gamma^e + \gamma^{vib}$) second dipole
 195 hyperpolarizability axial tensorial components of c-HfO₂ and YSH, respectively, computed
 196 with the PBE0 functional. All values are given in atomic unit and have been at the PBE0 level
 197 of theory applying the same basis sets we used for the geometry optimization.

c-HfO ₂	γ_{xxxx}^e		γ_{xxxx}^{vib}		γ_{xxxx}^{tot}	
	γ_{yyyy}^e	7.9×10^5	γ_{yyyy}^{vib}	~ 0	γ_{yyyy}^{tot}	7.9×10^5
	γ_{zzzz}^e		γ_{zzzz}^{vib}		γ_{zzzz}^{tot}	
3.2% YSH	γ_{xxxx}^e	6.5×10^5	γ_{xxxx}^{vib}	3.0×10^5	γ_{xxxx}^{tot}	9.5×10^5
	$\gamma_{yyyy}^e, \gamma_{zzzz}^e$	7.1×10^5	$\gamma_{yyyy}^{vib}, \gamma_{zzzz}^{vib}$	0.2×10^5	$\gamma_{yyyy}^{tot}, \gamma_{zzzz}^{tot}$	7.3×10^5
6.7% YSH	γ_{xxxx}^e	5.8×10^5	γ_{xxxx}^{vib}	3.2×10^5	γ_{xxxx}^{tot}	9.0×10^5
	$\gamma_{yyyy}^e, \gamma_{zzzz}^e$	6.5×10^5	$\gamma_{yyyy}^{vib}, \gamma_{zzzz}^{vib}$	0.3×10^5	$\gamma_{yyyy}^{tot}, \gamma_{zzzz}^{tot}$	6.8×10^5

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199 Hf atoms with Ytria and the creation of an oxygen vacancy. This structural distortion,
 200 clearly expressed by an elongated lattice constant *a* (see **Fig. 1**), activates several soft RAMAN
 201 active absorption bands that potentially could contribute in an additive manner to the supercell's
 202 second hyperpolarizabilities. In the present case, the vibrational contributions appear
 203 considerably strong in the direction of the most anisotropic tensorial component γ_{xxxx}^e ($\neq \gamma_{yyyy}^e \cong$
 204 γ_{zzzz}^e) which, in turn, corresponds to the most distorted lattice constant **a** (note that in the current
 205 case lattice constants **a**, **b** and **c** coincide with the *x*, *y* and *z* axes, respectively). Indeed, as seen
 206 by the values listed in **Table 3**, γ_{xxxx}^{vib} appears about fifteen and ten times greater than γ_{yyyy}^{vib} and
 207 γ_{zzzz}^{vib} or either 3.2% or 6.7% YSH, respectively. Finally, as seen by the displacement modes
 208 depicted in **Fig. 3** the low frequency acoustic modes which play a central role in the respective

209 vibrational contribution are in fact a mixture of antisymmetric oxygen displacements. For
 210 instance, at the PBE0 level of theory the contribution of the mode highlighted for 3.2%YSH
 211 contributes up one third ($\sim 1.0 \times 10^5$ au) of the overall γ_{xxxx}^{vib} value.



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213 **Fig.3.** RAMAN spectra of 3.2%YSH and 6.7%YSH (right) and computed displacement vectors of soft
 214 vibrational modes contributing the most on the vibrational supercell hyperpolarizabilities. All computations
 215 have been permed at the PBE0 level of theory.

216

217 3. Conclusion

218 In this work, the structural, electronic, and optical properties of cubic HfO₂ and YSH bulk
 219 have been investigated by first-principles calculations. Our computational data suggest that the
 220 NLO capacity of YSH, should be comparable to YSZ recently studied both experimentally and
 221 theoretically by Marcaud *et al.* In addition, by applying a newly developed method, recently

222 implemented in CRYSTAL17, it has been exposed that the electronic properties of YSH do not
223 constitute subjects of strong spin orbit coupling effects. Finally, strong evidence of significant
224 vibrational contributions to the optical nonlinearities of the systems have been found. An article
225 addressing in more details these effects is in preparation.

226

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