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Hassan Denawi, Jacques Demarais, C.S. Praveen, Michel Rérat, Panaghiotis Karamanis. Third order non-linear optical susceptibilities ( $\chi 3$ ) of yttria stabilized cubic hafnium(IV) oxide. Chemical Physics Letters, 2021, 785, pp.139157. 10.1016/j.cplett.2021.139157. hal-03418749

# HAL Id: hal-03418749 https://univ-pau.hal.science/hal-03418749

Submitted on 26 Nov 2021

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### Third Order Non-Linear Optical Susceptibilities ( $\chi^{(3)}$ ) of Yttria Stabilized 1 2 CUBIC HAFNIUM(IV) OXIDE

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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.

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#### 19 1. Introduction

The key to harness light's nonlinear effects and to unlock its "limitless" potential in 20 telecommunication technologies lies in the successful and cost-effective fabrication of fully 21 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, 3] routinely designated as  $\chi^{(3)}$ . The latter band-gap dependent property provides the means to 26 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 with the NLO behavior of yttria stabilized zirconia (YSZ). As demonstrated in that work, YSZ, 30 that can be grown epitaxially[6] on silicon substrates, features a comparable third order 31

nonlinear effective Kerr coefficient  $(n_2)$  with silicon nitride.[7] The latter material although it is one of the materials of choice for integrated photonics it suffers from significant shortcomings due to strong two photon absorption (TPA) effects that induce significant optical losses (see ref [5] and references therein). As Marcaud *et al.* concluded, TPA loses in YSZ are expected to be negligible thanks to its large bandgap and its quasi-cubic local atomistic structure. [5]

38 Motivated by the intense technological interest in the optical properties of functional oxides for integrated photonic devices worldwide, in this article, we report on reliable  $\chi^{(3)}$  estimations 39 of another widely recognized functional oxide, namely, yttria stabilized hafnia (YSH). Hafnia 40 41 (HfO<sub>2</sub>),[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<sub>2</sub>) is of great interest in CMOS technologies owed to its high dielectric constant and wider band gap. [10] However, cubic hafnia becomes "functional" only in quite high temperatures 44 (> 2500 °C)[11] and this impedes its application in many areas including optoelectronics. 45 46 Therefore, its stabilization at ambient conditions via doping is one of the preferred options. For 47 this task, Y<sub>2</sub>O<sub>3</sub> has proven a highly effective doping agent since it "stabilizes" hafnia's cubic phase even in relatively low concentrations ranging from 0.6 mol% to 6.5 mol%. In particular, 48 the current work reports on accurate coupled perturbed electronic static  $\chi^{(3)}_{iiii,iiii}$  macroscopic 49 data defined as: 50

51 
$$\chi^{(3)}_{iiii,iijj} = 2\pi \gamma^{e}_{iiii,iijj} (3V)^{-1}$$
 (where, i and j are the cartesian cell axes)

52 In Eq. (1)  $\gamma^e$  is electronic contribution of the second hyperpolarizability per unit cell volume 53 (V). The latter quantity can be determined experimentally<sup>7</sup> via measurements of the refractive 54 index:  $\hat{n}_2 = 3\chi^{(3)} (4c\epsilon_0\epsilon)^{-1}$  ( $\epsilon$  is the relative dielectric in-plane  $\epsilon_{xx}$  component,  $\epsilon_0$  the 55 electric permittivity of vacuum and c the light velocity and  $\chi^{(3)}$  is the effective third order 56 susceptibility[5]).



# 57 2. Results and discussion58

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Fig. 1. Relaxed stoichiometric atomistic super-cells YSH. All structures are true minima of the correspondingsupercell potential energy super-surfaces.

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

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

Table 1. Energy Band Gaps (Eg, in eV) of HfO<sub>2</sub>, YSH and YSZ, obtained within a plane wave and crystalline orbital calculations.

	PBE	PBE0	B3LYP
c-HfO <sub>2</sub>	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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The relaxed stoichiometric atomistic super-cell structure of c-HfO<sub>2</sub> ( $2 \times 2 \times 2$ ) as well as two 82 cells of YSH of the same size containing 3.2 and 6.7 mol% of Y<sub>2</sub>O<sub>3</sub>, (hereafter (3.2%, 6.7%)) 83 84 YSH), considered in this report are illustrated in Fig. 1. Our structural results for c-HfO<sub>2</sub>, also shown in the latter figure, are in good agreement with previously theoretical and experimental 85 outcomes reported by Zhao and Vanderbilt [17] within the local density and generalized 86 gradient approximation and close to the experimental value [18] of 5.08 Å per unit cell (10.16 87 88 Å for a  $2 \times 2 \times 2$  supercell). According to our knowledge up until now, no experimental or theoretical structural data have been reported for either concentration of YSH. 89

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

1. As expected, PBE functional, the least expensive computational method used here in, delivers
considerably smaller bandgaps with respect to the two hybrids PBE0 and B3LYP. A direct
comparison of our computed band gap of c-HfO<sub>2</sub> with spectroscopic ellipsometry
measurements of 5.8 eV reported by C. Adelmann *et al.* [19] reveals that the two hybrids, PBE0
and B3LYP, predict considerably improved bandgap energies lying about 0.7 and 0.2 eV above
the experiment, respectively. We expect similar method behavior for YSH phases considered
in this work.

As far as it concerns the dependence of YSH bandgap on the doping concentration, 99 100 our computational outcomes, clearly suggest that doping c-HfO<sub>2</sub> with yttrium induces a 101 noticeable bandgap broadening. The observed evolution is in accord with the trend reported by Chen et al [20] who studied the dependence of  $Y_2O_3$  concentration on the optical properties 102 103 of crystalline HfO<sub>2</sub> 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 and Hf we used a fully relativistic effective core potential (ECP) including both the scalar-108 109 relativistic AREP and the spin-orbit SOREP parts, developed by Peterson et al. [27] and Figgen et al.[28]. For Y, an associated valence basis set of triple-zeta quality was available for 110 solid-state calculations reported by Laun et al. [29] In the case of Hf, the basis set applied was 111 112 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 basis set is available at CRYSTAL basis set library [30] For O we used the basis set fromHeifets et al. [31]

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



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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137Table 2. Electronic contribution to the dielectric  $\epsilon_{xx}$ ,  $\epsilon_{yy=zz}$  components, to the third138order susceptibilities  $\chi^{(3)}_{xxxx}$ ,  $\chi^{(3)}_{yyyy=zzzz}$ ,  $\chi^{(3)}_{yyzz}$  components (×10<sup>-21</sup> $m^2V^{-2}$ ), of HfO<sub>2</sub>,139YSH 3.2% and 6.7% mol.in Y<sub>2</sub>O<sub>3</sub> and YSZ 6.7% mol. in Y<sub>2</sub>O<sub>3</sub>. In this case x, y and140z are placed parallel to the lattice constants a, b and c, respectively.

		$\epsilon_{xx} = \epsilon_{yy} = \epsilon_{zz}$		$\chi_{xxxx}^{(3)} = \chi_{yyyy}^{(3)} = \chi_{zzzz}^{(3)}$		$\chi^{(3)}_{yyzz}$
- 140	PBE0	3.8			0.9	
с-ню <sub>2</sub>	B3LYP	3.9			1.1	
		$\epsilon_{xx} = \epsilon_{yy}$	$\epsilon_{zz}$	$\chi^{(3)}_{xxxx}$	$\chi^{(3)}_{yyyy} = \chi^{(3)}_{zzzz}$	$\chi^{(3)}_{yyzz}$
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
0.770 1511	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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142 Let us now turn our attention to **Table 2** that summarizes our analytical CPKS outcomes of 143 the dielectric components and the electronic part of the third order NLO susceptibilities of 144 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 145 cubic phase. This trend is also followed by the computed third-order susceptibilities. Moving 146 147 now to the properties of interest we see that for all systems both functionals yield third-order susceptibilities not far from the limit of  $10^{-21}m^2V^{-2}$  which is considered adequate for certain 148 149 photonic applications [5]. In addition, it becomes evident that yttrium doping delivers a slight decrease in  $\chi^{(3)}_{yyyy}$ ,  $\chi^{(3)}_{zzzz}$  and  $\chi^{(3)}_{yyzz}$  components, a result that is in accord with the evident 150

bandgap widening occurring upon Y doping due to the inverse proportionality of  $\chi^{(3)}$  to the 151 bandgap of a given material. If we now directly compare the third order nonlinearities of 152 153 6.7% YSH to its zirconia analogue, that in this case shares the same local atomistic structure, it is revealed that both lattices feature  $\chi^{(3)}$  values of a similar order of magnitudes with the latter 154 being about two times more hyperpolarizable than the former. The revealed ordering is in 155 156 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 have used the tensorial components shown in Table 2 to calculate the effective Kerr coefficient 158  $\hat{n}_2$  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 159 at B3LYP level, lies about 1.6 times lower than the effective Kerr coefficient of 6.7% YSZ 160 161 obtained at the same level of theory.

162 Bearing in mind that the nonlinearities discussed so far correspond to the electronic part of  $\chi^{(3)}$ , one should regard the nonlinear coefficients listed in **Table 2** as the lowest limit at each 163 level of theory. Based on previous results for YSZ, we expect that the actual NLO response of 164 165 YSH should be even stronger owed to a combination of effects related to the frequencies of the applied dynamic or oscillating electric fields (c.c. frequency dispersion), possible thermal 166 167 lattice expansions, and more importantly to vibrational contributions.[32] To address the latter effects we relied on the variation of the dipole polarizability of each unit cell with respect to 168 169 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 infinitefrequency approximation, [33] the harmonic diagonal vibronic contribution is simplified as: 172

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

In Eq. (2) N is the number of atomic centers comprised in the unit cell and  $\frac{\vartheta \alpha_{xx,yy,zz}^e}{\vartheta \alpha_{xx,yy,zz}}$  the 174 derivative of the axial dipole polarizability component per unit cell with respect to the harmonic 175 normal  $Q_k$ -mode with  $\omega_k$ -frequency. The obtained analytical outcomes within the CPKS 176 177 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 computations at the PBE0 level expose a strong vibrational contribution of  $3.0 \times 10^5$  and  $3.2 \times 10^5$ 179 180 a.u. along the x-axis of the unit cells of 3.2% YSH and 6.7% YSH, respectively. As a result, a  $\gamma_{xxxx}^{tot}$  value of 9.5×10<sup>5</sup> a.u. which lies about 1.5 times higher than the corresponding  $\gamma_{xxxx}^{e}$  value 181 182 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 a careful analysis of the simulated RAMAN spectra shown in Figure 3. Thereby, we see that 186 187 the spectrum of pure cubic hafnia is characterized by a single strong absorption band at 640cm<sup>-</sup> 188 <sup>1</sup>. 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 attributed to the weak but evident deviation from the cubic symmetry of the doped YSH 192 193 supercell due to the replacement of two

Table 3. Unit cell electronic ( $\gamma^e$ ), vibrational ( $\gamma^{vib}$ ), and total ( $\gamma^{tot} = \gamma^e + \gamma^{vib}$ ) second dipole hyperpolarizability axial tensorial components of c-HfO<sub>2</sub> and YSH, respectively, computed with the PBE0 functional. All values are given in atomic unit and have been at the PBE0 level of theory applying the same basis sets we used for the geometry optimization.

c-HfO2	$\gamma^{e}_{xxxx}$ $\gamma^{e}_{yyyy}$ $\gamma^{e}_{zzzz}$	7.9×10 <sup>5</sup>	$\begin{array}{l} \gamma_{xxxx}^{vib} \\ \gamma_{yyyy}^{vib} \\ \gamma_{zzzz}^{vib} \end{array}$	~0	$\gamma_{xxxx}^{tot}$ $\gamma_{yyyy}^{tot}$ $\gamma_{zzzz}^{tot}$	7.9×10 <sup>5</sup>
3.2% YSH	$\gamma^{e}_{xxxx}$ $\gamma^{e}_{yyyy}, \gamma^{e}_{zzzz}$	6.5×10 <sup>5</sup> 7.1×10 <sup>5</sup>	$\gamma_{xxxx}^{vib}$ $\gamma_{yyyy}^{vib}$ , $\gamma_{zzzz}^{vib}$	3.0×10 <sup>5</sup> 0.2×10 <sup>5</sup>	$\gamma_{xxxx}^{tot}$ $\gamma_{yyyy}^{tot}, \gamma_{zzzz}^{tot}$	9.5×10 <sup>5</sup> 7.3×10 <sup>5</sup>
6.7% YSH -	$\gamma^{e}_{xxxx}$ $\gamma^{e}_{yyyy}, \gamma^{e}_{zzzz}$	5.8×10 <sup>5</sup> 6.5×10 <sup>5</sup>	$\gamma_{xxxx}^{vib}$ $\gamma_{yyyy}^{vib}, \gamma_{zzzz}^{vib}$	3.2×10 <sup>5</sup> 0.3×10 <sup>5</sup>	$\gamma_{xxxx}^{tot}$ $\gamma_{yyyy}^{tot}, \gamma_{zzzz}^{tot}$	9.0×10 <sup>5</sup> 6.8×10 <sup>5</sup>

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199 Hf atoms with Yttria 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  $\gamma_{xxxx}^e \ (\neq \gamma_{yyyy}^e \cong$  $\gamma_{zzzz}^{e}$ ) which, in turn, corresponds to the most distorted lattice constant **a** (note that in the current 204 205 case lattice constants **a**, **b** and **c** coincide with the x, y and z axes, respectively). Indeed, as seen by the values listed in **Table 3**,  $\gamma_{xxxx}^{vib}$  appears about fifteen and ten times greater than  $\gamma_{yyyy}^{vib}$  and 206  $\gamma_{zzz}^{vib}$  or either 3.2% or 6.7% YSH, respectively. Finally, as seen by the displacement modes 207 208 depicted in Fig. 3 the low frequency acoustic modes which play a central role in the respective vibrational contribution are in fact a mixture of antisymmetric oxygen displacements. For instance, at the PBE0 level of theory the contribution of the mode highlighted for 3.2% YSH contributes up one third (~  $1.0 \times 10^5$  au) of the overall  $\gamma_{xxxx}^{vib}$  value.



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

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## 217 **3. Conclusion**

In this work, the structural, electronic, and optical properties of cubic HfO<sub>2</sub> 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
- theoretically by Marcaud *et al.* In addition, by applying a newly developed method, recently

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

vibrational contributions to the optical nonlinearities of the systems have been found. An article

addressing in more details these effects is in preparation.

226

# 227 Acknowledgments

- 228 Part of this work was granted access to the HPC resources of [CCRT/CINES/IDRIS] under the
- 229 allocations 2019-2020 2020-2021 [A0040807031] made by GENCI (Grand Equipement
- 230 National de Calcul Intensif). We also acknowledge the "Direction du Numérique" of the
- 231 "Université de Pau et des Pays de l'Adour" and the Mésocentre de Calcul Intensif Aquitain
- 232 (MCIA) for the computing facilities provided. H. Denawi thanks ANR project FOIST. CSP
- acknowledges DST-India for INSPIRE Faculty Fellowship with award number IFA-18 PH217.
- JKD is grateful to the national science and engineering research council (NSERC) for a
- postdoctoral fellowship No. 545643. The authors declare that they have no known competing
- financial interest.

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