Ta₂O₅ polymorphs: Structural motifs and dielectric constant from first principles

Wanda Andreoni^{1,a)} and Carlo A. Pignedoli^{1,2,a)}

¹IBM Research–Zurich, 8803 Rüschlikon, Switzerland

²Swiss Federal Laboratories for Materials Testing and Research, Empa, 8600 Dübendorf, Switzerland

(Received 20 December 2009; accepted 9 January 2010; published online 9 February 2010)

Using large-scale simulations based on density-functional theory we determine the structural properties of several polymorphs of tantalia, their vibrational spectra and dielectric properties. Our calculations indicate that structurally distinct configurations can coexist, having coordination polyhedra that are dissimilar or have different relative arrangements. Interpolyhedra vibrations are discovered to be responsible for sizable changes of the static dielectric constant from one polymorph to the other. Our results for the dielectric constant (both at high and low frequency) are in excellent agreement with experiment and provide an explanation for the different measured values and their claimed dependence on growth conditions. © 2010 American Institute of Physics.

[doi:10.1063/1.3308475]

The pentoxide of tantalum (Ta₂O₅), also known under the name of tantalia or tantala, is a uniquely versatile material with a large number of technological applications, e.g., as dielectric resonator in microwave communication devices,¹ for antireflective coatings in solar cells,² as charge capacitor in DRAM devices,³ as gate dielectric in low-voltage organic thin-film transistors,⁴ and as photocatalyst.⁵

Its most prominent characteristic is the high (static) dielectric constant ϵ_0 , whose value however is not well defined but is reported to span an unusually large range, from ~ 25 to 100 ,^{6–12} depending, in particular, on the sintering temperature for the ceramic powders⁹ and on annealing conditions for thin films (TF).^{6,7,10–12} In principle, such a remarkable variation would be consistent with a dielectric constant dominated by the ionic polarisability as is the case for other high- k oxides (see, e.g., Refs. 13–15) and the observation of several dissimilar polymorphs for (bulk) crystalline phases.^{16–20} However, apart from attempts to rationalize this behavior as reflecting a simple correlation with the atomic density of the Clausius–Mossotti type,²¹ no clue exists regarding the link between structural characteristics and dielectric constant in Ta₂O₅.

The purpose of this letter is to understand in which way the structure influences the dielectric constant in Ta₂O₅, with the aid of large-scale simulations based on density-functional-theory (DFT) and linear-response theory.²² The first and challenging step of this study was to investigate the structural properties of several polymorphs of tantalia and determine their vibrational spectra (in the harmonic approximation), which is critical to assess their relative stability. The uncommon advantages of our calculations²³ were the unusually large size (224 or 462 atoms) of the models employed allowing for a flexible, accurate, full-scale geometry optimization. This scheme allows us to provide a reliable characterization of the preferred structural features of the material, unravel which phonons are responsible for the high values of the dielectric constant, and thus reveal the origin of possible variations in the ϵ_0 of different polymorphs, which does not have an analog in previously studied high- k oxides.

There is a rich literature on the structural properties of tantalia, which however does not provide an exhaustive and consistent description of the various crystalline polymorphs. In the past decades, a number of models have been proposed for the low-temperature crystal modifications (L-Ta₂O₅), derived from x-ray powder diffraction data. Extensive studies by Roth and his group invariably resulted in models containing impurities and/or vacancies. In their most recent study,²⁰ a single crystal was used for the first time; its composition includes a 0.14 wt Li and interstitial Ta atoms. In analogy with a previous model,¹⁷ the one in Ref. 20 shows the coexistence of two types of Ta–O coordination, with Ta at the center of either a pentagonal bipyramid (CN=7) or an octahedron (CN=6). In the model of Ref. 17, stoichiometry was ensured by partial occupation of specific oxygen sites. Given that the structural motifs were the same, and that the geometry given in Ref. 17 was easier to model, we used the latter as our starting coordinates for the optimization of the low-temperature structure, which we denote LT(O). This corresponds to an orthorhombic unit cell with 11 formula units. Another orthorhombic structure (β -Ta₂O₅) proposed for L-Ta₂O₅ has no vacancies and no impurities¹⁹ and a much smaller unit cell containing only two units. A hexagonal modification (δ -Ta₂O₅), originally observed more than 40 years ago,⁶ was also apparently resolved in Ref. 18. The Ta–O co-ordination polyhedra are exclusively of the octahedral type in the model proposed for β -Ta₂O₅ and also dodecahedral (CN=8) in δ -Ta₂O₅. There is a general consensus on the existence of a high-temperature orthorhombic phase (α -Ta₂O₅),²⁴ and some references to a monoclinic structure exist, whose parameters correspond to a slightly distorted orthorhombic one.²⁵ As-deposited TF are amorphous, but become polycrystalline after annealing. Depending on the annealing history, structures with orthorhombic^{6,7,26,27} or hexagonal¹⁰ symmetry were observed. Also in TF, a monoclinic modification was hypothesized as well as its transformation to an orthorhombic one, from the analysis of Raman spectra.²⁸

The only theoretical results available are from DFT calculations of the δ (Refs. 18 and 29) and β (Ref. 29) crystalline phases. When using the same unit cells (with two Ta₂O₅

^{a)}Electronic addresses: and@zurich.ibm.com and carlo.pignedoli@empa.ch.

TABLE I. Supercell parameters; volume V_0 per formula unit; energy E per formula unit relative to LT(O); static and high-frequency dielectric constant.

	LT(O)	O1	O2	H
a (Å)	40.4304	15.2535	14.7907	15.0652
b/a	0.3148	0.8339	0.8469	0.9732
c/a	0.2898	0.9915	1.0495	1.0132
α (deg)	89.9	90.2	90.1	90
β (deg)	90	90	90	90.1
γ (deg)	90	87.5	88.7	119.1
V_0 (Å ³)	91.358	91.606	89.844	92.021
E (eV)	0.0	0.11	0.01	0.17
ϵ_0	34	33	42	44
ϵ_∞	4.6	4.7	4.8	4.7

units) as in Refs. 18, 19, and 29, and k -point sampling in the Brillouin zone (BZ) for the geometry optimization, our calculations showed an intrinsic instability of those models (i.e., imaginary frequencies). Refs. 18 and 29 could not detect it, because symmetry constraints were imposed in the optimization of the internal coordinates, and no analysis of the vibrational spectra was performed. This finding led us to change the strategy and explore the structural properties of tantalia using relatively large supercells as periodically repeated units (of which we retain only $k=0$ in the BZ) and optimizing their lattice parameters under no symmetry constraint, simultaneously with the internal atomic coordinates. The supercells ($2 \times 4 \times 2$) were therefore triclinic, but the optimization resulted in very small distortions with respect to the original hexagonal and orthorhombic symmetries. The results are given in Table I. We refer to the former as sample H; samples O1 and O2 correspond to two different geometries obtained starting from the replicated β -unit cell: O1 is the result of local optimization of the internal coordinates, whereas O2 used simulated annealing followed by local minimization procedures. We also studied the model proposed in Ref. 17 [sample LT(O) in Table I] using a triclinic $1 \times 2 \times 3$ supercell, corresponding to 66 formula units. Distortions with respect to the orthorhombic symmetry turned out to be negligible.

Figure 1 shows the arrangement of the polyhedra centered on Ta, resulting from our simulations of the samples in Table I. Compared with the original models, there is no noticeable change for the LT(O) regarding the type of coordination polyhedra, whereas in the O2 as well as in the O1 sample (data not shown) one can recognize the formation of pentagonal bipyramids, in analogy with the low-temperature

FIG. 1. (Color) Ta–O coordination polyhedra arrangements in LT(O) (top), O2 (bottom left), and H (bottom right).

FIG. 2. (Color) Example of bond network (O1). Numbers correspond to the deviations from 180°.

structure. In the H sample, the dodecahedra are truncated owing to a distortion of the Ta coordination shell and corresponding formation of linear Ta–O–Ta units (the angle varies from 133° to 180°). Indeed sizable changes take place in samples H, O1, and O2 with respect to the initial coordinates, which explains the instability found for the “ideal” β - and δ -models as mentioned above. An example is the deviation from linearity of –Ta–O–Ta– chains as seen in Fig. 2.

The hexagonal structure (H) is the highest in energy. The values calculated for the vibrational entropy result in a free energy contribution of about 0.1 eV at room temperature for all three samples; the three slightly distorted orthorhombic models differ by less than 1 meV, the H model by ~ 5 meV, which reduces the difference between H and O1 even further. Given the small energy differences involved, however, the ordering may well depend on the choice of the exchange-correlation functional [see Ref. 29]. We can however consider these results a strong indication that dissimilar configurations corresponding to orthorhombic lattices (with slight distortions) may coexist, at room temperature, and that hexagonal polymorphs may be favored by entropic effects.

The calculated value for ϵ_∞ [in the range 4.6–4.8 (Table I)] is clearly insensitive to the structure and corresponds well to the measured refractive index of approximately 2.2 (Refs. 27 and 28) (which gives $\epsilon_\infty^{\text{exp}} \sim 4.8$). This behavior is similar to that obtained for other high- k oxides.^{13–15} In all four cases, we find a highly anisotropic dielectric constant owing to its lattice component.³⁰ The average values are reported in Table I. For two samples [LT(O) and O1] the average lattice component ϵ_L is about 29 and for the other two (O2 and H) about 38. Not surprisingly, ϵ_L can differ in different polymorphs, but the mechanism we have identified that explains discrepancies of as much as ten is not simply related to a change of atomic density and does not resemble anything found for other high- k oxides. In compounds such as Al_2O_3 or aluminates or HfO_2 or, even more strikingly, HfSiO_4 ,¹⁵ variations of ϵ_L on passing from one structure to the other were determined by the change in local characteristics, be it either the coordination shell or geometric peculiarities. In contrast, all four samples of Ta_2O_5 show the predominance of the octahedral coordination, and, whenever present, the sevenfold coordination does not correspond to a strongly different environment. The peculiarity of the dielectric response of Ta_2O_5 emerges in the analysis of the vibrational structure.

FIG. 3. (Color online) Lattice contribution to the dielectric constant integrated over the IR range of frequencies.

Figure 3 reports the contributions from the optically active phonons to the lattice component, integrated over the frequency range from ~ 20 to 900 cm^{-1} . We deduce that the difference between LT(O); O1 on one side and O2; H on the other, is largely due to the low-frequency modes with $\omega \leq 100\text{ cm}^{-1}$. The rest of the spectrum globally contributes the same amount in all four samples. This finding is interesting if the nature of the modes is understood: The highest frequency range corresponds to Ta–O stretching modes ($600\text{--}800\text{ cm}^{-1}$) that do not contribute to the dielectric constant. Rocking and bending modes—also coupled—lie in the intermediate range of the spectrum and correspond to the predominant contribution. Interestingly, the latter is largely structure insensitive, reflecting the fact that in all samples the local environment of a Ta or an O are very similar. The discrepancy between the two sets of values we find for ϵ_L comes from the vibrations in the range $20 \leq \omega \leq 100\text{ cm}^{-1}$, which, as we have verified, can be mainly associated with relative motions of polyhedra (see Fig. 1) taken as a whole. We shall call them “inter-polyhedra modes.” Unfortunately, no measurement of IR spectra below 400 cm^{-1} is available.³¹ However Raman spectra^{27,28} reveal several features in the far-IR that could not be interpreted in terms of vibrations “internal” to the coordination polyhedra but ascribed²⁸ to the interaction of the latter with hypothesized “external” clusters. Our results contrast with this speculation and reveal the origin of these modes.

Comparison of our calculations for ϵ_0 in Table I with experiment can now be drawn. The value reported most frequently in the literature for crystalline tantalia is 25, but no reference to specific data is given. An $\epsilon_0 \sim 24\text{--}25$ indeed is measured in as-deposited TF (Refs. 7 and 10) that are amorphous. Measurements on polycrystalline powder ceramics are typically ~ 35 (Refs. 8 and 9) at low temperatures and tend to increase with increasing temperature. This corresponds well with our results. In TF, crystallization after annealing always resulted in an increase of the dielectric constant. Effective values were derived ranging from 30 (Ref. 6) to 45,⁷ 46–52,¹¹ 56–59,¹⁰ and even to 90–110.¹²

In conclusion, our study has helped to identify the preferred structural motifs of tantalia, to unravel the nature of the low-frequency phonons as associated to the inter-polyhedra interaction, and to reveal an unforeseen mechanism that may explain the scattering in the measurements of the static dielectric constant and is intrinsic to the material. Configurations having dissimilar arrangements of the coordi-

nation polyhedra can coexist at room temperature. Moreover, employing different growth conditions may easily favor either one or the other; in some cases, this may correspond to a sizable discrepancy in the response in the far-IR and in the values of the dielectric constant. In real systems, extrinsic mechanisms are also expected to be active in producing a variation of ϵ_0 , through defects such as local deviations from stoichiometry and impurities. In particular, even a modest enhancement in the IR intensity of the low-frequency inter-polyhedra modes could change ϵ_0 significantly.

¹R. J. Cava, *J. Mater. Chem.* **11**, 54 (2001).

²O. Sankur and W. Gunning, *Appl. Opt.* **28**, 2806 (1989).

³E. Atanassova and A. Paskaleva, *Microelectron. Reliab.* **47**, 913 (2007).

⁴C. Bartic, H. Janse, A. Campitelli, and S. Borghs, *Org. Electron.* **3**, 65 (2002).

⁵Y. Zhu, F. Yu, Y. Man, Q. Tian, Y. He, and N. Wu, *J. Solid State Chem.* **178**, 224 (2005).

⁶G. S. Oehrlein, F. M. d’Heurle, and A. Reisman, *J. Appl. Phys.* **55**, 3715 (1984).

⁷A. Pignolet, G. M. Rao, and S. B. Krupanidhi, *Thin Solid Films* **258**, 230 (1995).

⁸R. J. Cava, W. F. Peck, and J. J. Krajewski, *Nature* **377**, 215 (1995).

⁹R. J. Cava, J. J. Krajewski, W. F. Peck, Jr., and G. L. Roberts, *J. Appl. Phys.* **80**, 2346 (1996); R. J. Cava, J. J. Krajewski, *ibid.* **83**, 1613 (1998).

¹⁰C. Chanceliere, S. Four, J. L. Autran, R. A. B. Devine, and N. P. Sandler, *J. Appl. Phys.* **83**, 4823 (1998).

¹¹P. C. Joshi and M. W. Cole, *J. Appl. Phys.* **86**, 871 (1999).

¹²J. Lin, N. Masaaki, A. Tsukune, and M. Yamada, *Appl. Phys. Lett.* **74**, 2370 (1999).

¹³G.-M. Rignanese, F. Detraux, X. Gonze, A. Bongiorno, and A. Pasquarello, *Phys. Rev. Lett.* **89**, 117601 (2002).

¹⁴S. Shevlin, A. Curioni, and W. Andreoni, *Phys. Rev. Lett.* **94**, 146401 (2005).

¹⁵C. A. Pignedoli, A. Curioni, and W. Andreoni, *Phys. Rev. Lett.* **98**, 037602 (2007).

¹⁶N. Terao, *Jpn. J. Appl. Phys., Part 1* **6**, 21 (1967).

¹⁷N. C. Stephenson and R. S. Roth, *Acta Crystallogr., Sect. B: Struct. Sci.* **27**, 1037 (1971).

¹⁸A. Fukumoto and K. Miwa, *Phys. Rev. B* **55**, 11155 (1997).

¹⁹A. Aleshina and S. V. Loginova, *Crystallogr. Rep.* **47**, 415 (2002).

²⁰I. E. Grey, W. G. Mumme, and R. S. Roth, *J. Solid State Chem.* **178**, 3308 (2005).

²¹T. Busani and R. A. B. Devine, *J. Appl. Phys.* **98**, 044102 (2005).

²²S. Baroni, S. de Gironcoli, A. Dal Corso, and P. Giannozzi, *Rev. Mod. Phys.* **73**, 515 (2001).

²³CPMD V13.3 Copyright IBM Corporation 1990–2009; MPI für Festkörperforschung, Stuttgart, Germany, 1997–2001. Norm-conserving angular-momentum-dependent, scalar-relativistic pseudopotentials were used, derived with the Martins–Troullier method, N. Troullier and J. L. Martins, *Phys. Rev. B* **43**, 1993 (1991); in Ta 5s and 5p shells are treated as valence electrons, a 120 Ry cutoff was used for the plane-wave expansion of the electronic wavefunctions and the PBE, J. P. Perdew, K. Burke, and M. Ernzerhof, *Phys. Rev. Lett.* **77**, 3865 (1996); and **80**, 891 (1998) exchange-correlation functional.

²⁴A. S. Pavlovic, *J. Chem. Phys.* **40**, 951 (1964).

²⁵J. L. Waring and R. S. Roth, *J. Res. Natl. Bur. Stand.* **72A**, 175 (1968).

²⁶J.-Y. Zhang, Q. Fang, and I. W. Boyd, *Appl. Surf. Sci.* **138–139**, 320 (1999).

²⁷R. R. Krishnan, K. G. Gopchandran, V. P. Mahadevan Pillai, V. Ganesan, and V. Sathe, *Appl. Surf. Sci.* **255**, 7126 (2009).

²⁸P. S. Dopal, R. S. Katiyar, Y. Jiang, R. Guo, and A. S. Bhalla, *J. Raman Spectrosc.* **31**, 1061 (2000).

²⁹B. R. Sahu and L. Kleinman, *Phys. Rev. B* **69**, 165202 (2004).

³⁰See supplementary material at <http://dx.doi.org/10.1063/1.3308475> for the dielectric matrices of the four samples.

³¹We note that the experimental evidence for vibrational density at 1300 or 2000 cm^{-1} pointed out in H. Ono and K. Koyanagi, *Appl. Phys. Lett.* **77**, 1431 (2000) finds no correspondence in our calculations. These features should be attributed to impurities in the bulk or at the interface with the substrate.