Conservation of dielectric constant upon amorphization in perovskite oxides

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(Dated:)

We report calculations indicating that amorphous RAO3 oxides, with R and A trivalent cations, have approximately the same static dielectric constant as their perovskite crystal phase. The effect is due to the disorder-activated polar response of non-polar crystal modes at low frequency, which compensates a moderate but appreciable reduction of the ionic dynamical charges. The dielectric response was studied via density-functional perturbation theory. Amorphous samples were generated by molecular dynamics melt-and-quench simulations.

PACS numbers: 77.22.d,63.20-e,78.30-j,61.66-f

I. INTRODUCTION

In the context of integrated microelectronics there is a clear dichotomy, rooted in the fundamentals of dielectric screening, between crystalline and amorphous dielectric layers. The latter are preferable in terms of electrical leakage behavior, but their dielectric response may be unsatisfactory for applications requiring a large static dielectric constant $\kappa_s$. A case in point is that of the so-called high-$\kappa$ materials, gradually replacing silica as gate dielectric in aggressively downscaled Si-based integrated microelectronics. It is unclear in general if the high $\kappa$ of a crystal compound will be conserved in its amorphous phase. This is due to the nature of the dielectric screening in high-$\kappa$ materials, where the total static dielectric constant $\kappa_s=\kappa_{\infty}+\kappa_{\text{ion}}$ is dominated by the lattice-vibrational component $\kappa_{\text{ion}}$, being typically a factor 2 to 10 larger than the electronic $\kappa_{\infty}$. Large values of $\kappa_{\text{ion}}$ are due to large effective charges and soft infrared (IR) vibrational modes. This is borne out by its definition:

$$\kappa_{\text{ion}}^{\alpha\beta} = \frac{4\pi e^2}{\Omega} \sum_{\lambda} \frac{z_\lambda \alpha z_\lambda \beta}{\omega_\lambda^2}, \quad z_\lambda = \sum_{i\beta} \frac{Z_{i,\alpha,\beta}^* \xi_{i,\lambda,\beta}}{\sqrt{M_i}},$$

with $z$ the mode charge vector, $\Omega$ the system volume, $Z_{i,\alpha,\beta}$ the effective or dynamical or Born charge tensor and $M_i$ the mass of atom $i$, $\xi_{i,\lambda,\beta}$ and $\omega$ the eigenvector and eigenfrequency of mode $\lambda$ at zero wave-vector, and $\alpha$, $\beta$ cartesian indexes.

Dynamical charges are termed “anomalous” if they exceed the nominal ionicity. Such “anomaly” (sort of a misnomer, being ubiquitous and dramatic in many oxides) results from a subtle interplay of covalent and ionic bonding, as discussed in detail in Ref.[5]. Lattice disorder will generally reduce the efficiency of orbital overlap and, hence, the dynamical charge flow measured by the dynamical charges. Thus the $Z^*$’s are expected to decrease in the disordered amorphous environment. On the other hand, softer IR-active modes counterbalancing this effect (through the $1/\omega^2$ factor in Eq. 1) may appear in the amorphous phase (they indeed do, both in the present case as well as in zirconia, as reported in Ref.[6]). The major reason for this is that IR-active and inactive modes are not discriminated by symmetry constraints as in the crystal phase, so that non-IR crystal modes, or remnants thereof, can acquire IR activity. For sufficiently low frequency, thanks to the $1/\omega^2$ factor in Eq. 1, even weakly IR-active modes may produce a large dielectric intensity (counterbalancing the general decrease in $Z^*$) and cause a conservation or a boost of the dielectric constant.

From the discussion so far, it is apparent that a quantitative assessment of the dielectric constant ingredients is central to evaluating a technologically relevant dielectric. Indeed, if the amorphous phase of a given material has a similar ionic screening as its crystal phase, there is hardly any point in pursuing the fabrication of single-crystal layer of that material.

Here we study from first principles the static dielectric response in amorphous high-$\kappa$ RAO3 oxides with A, R trivalent cations. We show that indeed the dielectric constant in the amorphous phase is similar to that of their distorted-perovskite crystal phase, due to a moderate reduction in polarizability, and to the disorder-induced IR activation of non-polar low-energy modes of the crystal.

Our specific case studies are LaAlO3 and DyScO3. We described previously their crystal properties.2,4 The nomenclature ”R” for the larger, nominally 12-fold coordinated cation and ”A” for the octahedrally-coordinated one is used throughout the paper. These two compounds represent quite thoroughly the relevant trivalent-cation perovskites RAO3 for high-$\kappa$ applications. Indeed, the choice of A can be restricted to either Al or Sc because rare-earths, Lu, La, and Y function as the R cation, mixed-valent Ti and Mn cause small gaps and correlation2,4 and Ga is analogous to Al in this stoichiometry.2,25 Both materials are actively studied by the high-$\kappa$ community, and both have been reported to have high dielectric constants (~25) in the crystalline as well as the amorphous state. In DyScO3 the effect is so far unconventional. A report also exists of a sizable (40%) deterioration of the dielectric constant in LaAlO3. While not aiming at a definite resolution of this issue,
here we find that a conservation of dielectric screening in these materials is plausible from the theoretical point of view.

II. TECHNICAL MATTERS

Amorphous LaAlO$_3$ and DyScO$_3$ samples were generated by a melt-and-quench molecular dynamics procedure, using the empirical-potential GULP code. A liquid was equilibrated at temperature $T=5000$ K for 30 ps to achieve fully randomized cation positions. It was then quenched by Nose constant-T dynamics at 50 K/ps. 2-ps constant-T intervals separated by abrupt 100 K down-steps were used down to 2000 K. After that, since the mobility was then very low, larger down-steps of 500 K and simulation periods up to 5 ps were used down to 500 K, whereby structural properties (expected to be well converged at this cooling rate) were sampled in a 5 ps run.

For LaAlO$_3$, we also ran ab initio density-functional constant-T dynamics with the VASP code to quench the equilibrated liquid from 5000 to 50 K with alternating 0.5- ps constant-T intervals and 0.5 ps, 500 K ramp-down segments. The differences in structural properties in the two approaches are moderate and affect the dielectric properties slightly (see the discussion below). Cell sizes (80 atoms for ab initio dynamics, 80 to 320 atoms for empirical) do not influence the structure appreciably.

After cooling to 0 K by damped dynamics, we further relaxed the structure using the ab initio Espresso code (finding, incidentally, no major changes in structure or density). On the final structure, the Espresso code was used to perform linear-response density-functional perturbation theory calculations of electronic dielectric constant, effective charges and $k=0$ phonon modes, building up the dielectric constant (Eq. 1). All DFT calculations are done within the generalized-gradient approximation (for details see 14,15), and will be indicated henceforth by the acronym GGA.

III. RESULTS AND DISCUSSION

A. Structural properties

As no experimental structural data are available for the amorphous materials under consideration, a sanity check of our generated structures is to compare their properties with those of the crystal phase. The amorphous samples appear to inherit many structural characteristics of the crystal. Their main feature is the approximate conservation of an octahedral A-O backbone, though with somewhat different octahedra distortion and degrees of cation disorder in LaAlO$_3$ and DyScO$_3$. The structure-characterizing correlation function of the simulated amorphous samples are collected in Fig. 1. Preliminarily we note that the intermixing of cation sublattices (i.e A$_R$ antisites and such) is ruled out: no R→A cation exchange is observed in any of the simulations, and the hypothetical AlLaO$_3$ perovskite is metallic, 40% less dense and widely higher in energy than LaAlO$_3$.

Let us discuss Fig. 1. We refer to crystal or amorphous phases by the prefixes "c-" or "a-". In ideal perovskite the R (La, Dy) cation is 12-fold, and the A (Al, Sc) cation is 6-fold coordinated. The main feature of both a-phases is the A-O $g(r)$ function peaking neatly at typical A-O distances (Fig. 1) with a resulting A-O coordination of 6 as in the c-phases. The typical O-A-O (e.g. O-Al-O) angles are very close 90 and 180$^\circ$. As no experimental structural data are available for these materials is plausible from the theoretical point of view.
the large orthorhombic rotations. The Dy-O g(r) is also sharper than the La-O (Fig.1), suggesting a lesser degree of disorder of the Dy sublattice. The loss of coordination of La is also signaled by the O-La-O angle distribution (Fig.1), whose peaks at 60 and 120° are quite broadened but well-defined, whereas those at 90° and 180° are both washed out. This behavior is not unexpected as the ideal-perovskite angles are those internal to a cuboctahedron (60, 90, 120, and 180°): the 60° is the most robust as it corresponds to O pairs belonging to one single octahedron, and correlates with the 120°, as does the 90° with the 180° one.

Finally, the R-A functions show significant remnants of the correlation of the interpenetrating cubic sublattices of A and R cations in the c-phase: the g(r) main peak (Fig.1) is fairly well defined at the typical R-A distances, and the R-A-R angle function (Fig.1) still has a bimodal structure around the ideal-perovskite angles 70 and 110°.

B. Polarizability

With reference to Eq.1, we note that the dipoles z generated by atomic vibrations determine, along with the vibrational frequencies discussed below, the static dielectric constant (Eq.1). One key ingredient of these dipoles is the ionic dynamical polarizability, i.e. as the time-integrated current flowing upon unit displacement of a specific ion. An unbiased measure thereof is provided by the effective dynamical-charge tensor of atom i, $Z_\nu^{\alpha\beta} = \Omega / \epsilon (\partial P_\nu / \partial u_\beta)$, i.e. the derivative of the total polarization vector with respect to the vector displacement of atom i. A drop in dynamical charges implies therefore a reduction of the ionic dielectric activity (Eq.1).

We compare the present GGA dynamical charges, electronic dielectric constants, and total static dielectric constants with their crystal counterparts in Table I. To present the data synthetically, we average the a-phase charge tensors over all atoms of a given species, and decompose them thereafter into s, p, and d components (i.e. spherical, traceless symmetric, and traceless antisymmetric). The s component, accounting for about 98% and 95% of the tensor norm for cations and oxygen respectively, is reported in Table I for the amorphous case. In the same Table we also report the s component of the dielectric tensors (these are only very mildly non-isotropic). As we now discuss, the dynamical charges results of Table I are quite coherent with the structural properties described above, and with the general properties of the cations involved; charges on O largely adjust to obey dynamical charge-neutrality sum rules.

In a-LaAlO$_3$, Al has the same non-anomalous dynamical charge as in the crystal. This is a token of its having no covalent bonds to support a dynamical charge flow upon displacement in either case. Al also has a rather crystal-like environment with a coordination of 6 and average angle 90° (Fig.1a and 1b). For La, $Z^*$ is instead severely reduced: the disruption of ionic-covalent charge flow is clearly due to the major loss of coordination (12 to 6, see Fig.1c) also signaled by the O-La-O angle distribution in Fig.1d.

In a-DyScO$_3$ the effect is reversed. Dy has essentially the same $Z^*$ as in the crystal, in accordance with its having a similarly well-defined coordination and distance to O (Fig.1). Note also the O-Dy-O angle distribution, Fig.1d, quite less blurred than the O-La-O of a-LaAlO$_3$. The A cation, Sc, suffers instead from an appreciable $Z^*$ reduction. As we discussed in Ref. 4, Sc has a sizably anomalous effective charge in the crystal, as a results of its employing d states in bonding to O. While the Sc coordination is still 6 in a-DyScO$_3$, the covalent component of the dynamical polarizability is reduced by the strong octahedra distortion. We remind that the latter shows up in the bimodal angle distribution at 80 and 100° (Fig.1d) instead of a unimodal around 90°.

In closing this section we recall our earlier reports of a sizable reduction of DFT effective-charge anomalies upon use of self-interaction corrections. This reduction lead to total dielectric constants smaller by ~10-20%, the agreement with experiment being typically improved. Due to the size of the cells involved here, we did not evaluate the self-interaction-corrected charges in the present cases. The $\kappa$’s reported here may thus be expected to be somewhat larger than experiment. Of course, the amorphous-crystal comparison is unaffected.

C. Dielectric and vibrational properties

In Table II we reported the average electronic and static dielectric constants. The a-phase static values are clearly in the vicinity of the crystal values, as we originally purported to show. The electronic component is only slightly affected by disorder. Indeed, we find that both a-phases have a crystal-like gap in the electronic density of states, as expected in view of their strong ionicity and of the anion-like and cation-like character of, respectively, valence and conduction states. The ionic component, therefore, is also approximately the same in both phases. To understand why this occurs despite the reduced effective charges, we analyze the frequency-dependent dielectric intensity, i.e. the individual (dimensionless) terms in the first equality of Eq.1.

In Fig.2 we report the dielectric intensity (left panels)
and IR spectrum (right panels) of a-DyScO$_3$ (top panels) and a-LaAlO$_3$ (bottom panels). We indicated the approximate position of the calculated Raman, IR, silent modes of the crystals as horizontal bars superposed on the IR spectra of the a-phase. A detailed list is given in Refs. 2 and 4. In Fig. 3, we report the dipole amplitudes decomposed by atomic species, i.e., the vectors $z_i$ as defined in Eq.1, but obtained summing over one species only.

Considering the IR spectrum which, we recall, is a measurable quantity, we note that the IR activity at low frequency is small. However, it is amplified in the dielectric intensity due to the $1/\omega^2$ factor (Eq.1), so we concentrate on the low frequency region. To anticipate our conclusion, the dielectric enhancement at low frequency is due to IR-inactive (Raman, silent) or inefficient IR crystal modes that acquire IR character or enhance it due to disorder. (Inefficient IR modes in the crystal are those with weak intensity, say 3 orders of magnitude lower, than typical IR-active crystal modes – see Ref. 4.)

Aside from minor differences of detail, both c-LaAlO$_3$ and c-DyScO$_3$ have their dominant IR modes in the range 150-200 cm$^{-1}$ as discussed previously. These modes derive from the octahedron-vs-R sublattice vibration typical of perovskites. Further IR modes around 300 to 400 cm$^{-1}$ and above – relatively uninteresting for us, being suppressed by the $1/\omega^2$ factor in Eq.1 – are intra-octahedron vibrations involving only O and the A cation. These features largely carry over to the a-phases, as confirmed by the IR spectra (Fig. 3b and d) showing peaks in approximate correspondence with crystal IR activity regions. The species-projected dipoles (Fig. 3) also confirm this picture: in the 150-200 cm$^{-1}$ region the dipoles generated, respectively, by the R cation and the A-O complex, are similar as expected. At higher frequency, instead, the displacements are exclusively A and/or O-like, and have intra-octahedron character.

Let us discuss the low-frequency dielectric intensity-enhancing modes starting with LaAlO$_3$. We recall that in c-LaAlO$_3$ there exist three Raman modes (per primitive cell) related to the cubic-rhombohedral instability at 35 (doubly degenerate) and 130 cm$^{-1}$. They are characterized by octahedra rotations accompanied by non-dipolar R-cation vibrations. In the disordered environment these modes mix with the IR counter-phase R-(A-O) motions, producing new vibrations with non-zero IR activity. The energies of these mixed modes start at about 40 cm$^{-1}$, and boost the low-frequency dielectric intensity. The mixed modes can be seen as vibrations of the disordered R sublattice against A-O units wobbling in a disorderly fashion about their center. This agrees with the dipole at low frequency being mostly contributed by the R cation, as shown in Fig. 3a.

In c-DyScO$_3$, the relevant modes are Raman at 100 cm$^{-1}$, silent at 70 cm$^{-1}$, and inefficient IR also near 100 cm$^{-1}$. As we have discussed previously in Ref. 4, especially in connection with Fig. 3 thereof – these three modes have no dipole (or just a tiny one) thanks to a delicate symmetry-induced compensation of different displacements. As such, they have a potential for developing some dipole moment in a disordered environment disrupting the symmetric vibrational pattern. We therefore attribute the dielectric intensity boost at low frequency in
DyScO$_3$ to the activations of IR activity in these modes. Dy motions are again quite important in this energy region. A peculiarity of DyScO$_3$ is that Sc motions (Fig.3) die out at frequencies above 300–400 cm$^{-1}$ (unlike those of Al, Fig.3). We note in passing that this is probably a characteristic feature of Sc-O vibrations, as the dipoles die out at frequencies above 300–400 cm$^{-1}$ probably lower than for the empirical-potential sample (unlike those of Al, Fig.3).

We finally mention the results for the a-LaAlO$_3$ structure generated by ab initio dynamics. The static dielectric constant for this structure is 22.4. While still in the vicinity of the crystal value, this result is appreciably lower than for the empirical-potential sample (∼27). The decrease is due to a (moderate) reduction in the ionic dielectric intensity at low frequency (the electronic part is unchanged, at 4.5). The reduction should be attributed to the lower average coordination of Al sites by about 10% (5.4 vs 6) in the ab initio sample compared to the empirical-potential sample discussed so. We suspect this to be an artifact caused by the much higher cooling rate of the ab initio sample (500 K/psec) compared to the empirical-potential one (50 K/psec) discussed in detail so far. (We recall, anyway, that all samples were optimized in structure at 0 K after cooling.)

Summary and acknowledgments

In summary, we have shown that the static dielectric response in amorphous high-$\kappa$ RAO$_3$ oxides is similar to that of their crystal phase, due to a combination of moderate polarizability reduction and of disorder-induced IR activation of non-polar low-energy modes, as well as to the inheritance by the a-phase of several c-phase structural and vibrational features. We conclude that the dielectric-constant conservation upon amorphization of these materials is theoretically plausible. Given their very similar structural and vibrational properties at low frequency, we suggest that our conclusions may qualitatively apply to perovskites with cations from Group II and IV.

Work partially supported by EU (project FUNC), MUR Italy (PON-Cybersar, PRINO5, "Ritorno cervelli"), Fondazione Bds, IMEC industrial affiliation program. Most calculations were done on the high-performance cluster ichnusa@CASPUR Rome.

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