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Hybrid density functional theory LCAO calculations on phonons in Ba(Ti,Zr,Hf)O_3

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Phonon frequencies at the Γ, X, M, and R points of the Brillouin zone (BZ) in the cubic phase of Ba(Ti,Zr,Hf)O_3 were calculated by the frozen phonon method using density functional theory with the hybrid exchange correlation functional PBE0. The calculations use linear combination of atomic orbitals basis functions as implemented in the CRYSTAL09 computer code. The Powell algorithm was applied for basis-set optimization. In agreement with experimental observations, the structural instability via soft modes was found only in $BaTiO_3$. A good quantitative agreement was found between the theoretical and experimental phonon frequency predictions in $BaTiO_3$ and $BaZrO_3$. It is concluded that the hybrid PBE0 functional is able to predict correctly the structural stability and phonon properties in perovskites under consideration. The symmetry of phonons for nonzero **k** vector (X, M, and R points of the BZ) is given for each calculated phonon frequency, and it will be useful for future comparison of the calculated results with the experimental data on neutron scattering (such data are absent at present).

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I. INTRODUCTION

ABO_3-type oxides such as barium titanate, zirconate, and hafnate [$BaTiO_3$ (BTO), $BaZrO_3$ (BZO), and $BaHfO_3$ (BHO)] are attractive for various technological applications in modern electronics, nonlinear optics, and catalysis.[1–4] BTO has been widely investigated since the discovery of its ferroelectric properties. BZO has attracted a great deal of attention as a high-temperature protonic conductor with possible applications in fuel cells and hydrogen sensors. BHO gained wide interest as a ceramic material, a material with a high melting point, and because of its high thermal-expansion coefficient and high-k dielectric capacitor. The temperature dependence of the phase behavior is different in these three crystals.

At high temperature, BTO is stable in a paraelectric cubic structure with five atoms per unit cell (space group $Pm3m$). At lower temperatures, BTO has three phase transitions to ferroelectric phases. At 393 K, BTO undergoes a structural phase transition to a tetragonal (space group $P4mm$) ferroelectric phase. Below 278 and 183 K, BTO has an orthorhombic (space group $Amm2$) and rhombohedral (space group $R3m$) structure, respectively.[5] BZO and BHO have a perfect cubic structure ($Pm3m$) over a wide range of temperatures and do not undergo any structural phase transitions even down to 2 K.[5]

Once the electronic (ground) state of a system of nuclei and electrons is found, the free-energy temperature dependence can be analyzed. That is why exact knowledge of the vibrational states of a solid is the key to the calculation of it thermodynamic properties as a function of temperature.[6] This problem is solved in the first-principles density functional theory (DFT) calculations of the electronic structure and phonon frequencies in crystals.

There exist numerous experimental data explaining BTO ferroelectric behavior. However, our knowledge concerning the nature of ferroelectric phase transitions in BTO was rather limited until first-principles DFT calculations were employed to study BTO lattice dynamics. The first-principles full-potential linear augmented plane wave (LAPW)[7,8] and PW DFT[9–14] phonon spectra calculations on BTO cubic phase demonstrated its structural instability via soft modes with imaginary frequencies at the Brillouin zone (BZ) symmetry points Γ(0, 0, 0), X(0, 0, 0.5), and M(0,0.5,0.5).

Several DFT calculations have been reported on the electronic and atomic structure of bulk BZO.[15–20] The first-principles DFT calculations on phonons in BZO give contradictory results.[16] Indeed, the imaginary frequencies (instable modes) at the Γpoint were not found in DFT calculations[17,18] but appear in the results of other calculations.[16] The unstable mode at M was not found in Refs. 17 and 18 but appears in the results of calculations[16] performed using also the DFT method. The unstable mode at R was found in calculations from Refs. 16–18, in disagreement with the experimental data showing that BZO structure is cubic. It was concluded[16] that the examination of phonon instabilities and their consequences for structural symmetry are especially demanding of the quality of the exchange-correlation (XC) potential and pseudopotential being used to describe the interaction of the core and valence electrons—transferable small-core pseudopotentials (transferable rather than inexpensive) should be taken.

The first DFT calculations of BHO mechanical, electronic, and optical properties appeared only recently.[15,21–24] To the best of our knowledge, only one phonon DFT [local density approximation (LDA)] calculation has been published[21] for cubic BHO, and no imaginary frequencies were found, in agreement with the experimentally found stability of cubic BHO.

First-principles DFT calculations of the electronic and structural properties of perovskites are based in most cases on the LDA for the XC part of the density functional and to a lesser extent on the semilocal general gradient approximation (GGA), mainly in the parametrization of Perdew-Burke-Enzerhof (PBE).[25] It is well known that DFT in the LDA or the GGA is often better than the Hartree-Fock (HF) model, as the essential error of HF arises from the fact that in the HF model, the exchange-correlation hole in a two-electron bond is too delocalized.

The simple truth is not that the LDA or the GGA is particularly good, but that HF is rather poor in the two-electron chemical bond description. In the perovskites, such bonds arise between the transition metal and oxygen atoms, being important for the correct description of the crystal properties. To improve the LDA and GGA models, the orbital-dependent hybrid XC functionals (such as B3PW, B3LYP, and PBE0) are used. These functionals mix a fraction of HF exchange into the DFT exchange functional and use the DFT correlation part. Hybrid XC functionals are popular in molecular quantum chemistry as they have been shown to provide an accurate description of the bond lengths, atomization energies, and vibrational spectra for most molecules.[26,27] The B3PW and B3LYP functionals contain parameters that were optimized to fit the experimental data for molecules. In the past decade, these hybrid functionals have also been increasingly applied for solids.[28,29] The PBE0 hybrid functional[30] with the PBE exchange-correlation part is parameter-free as the percentage of HF exchange mixing with PBE exchange is found from the perturbation theory. The hybrid functionals have been applied to perovskites in very few cases.[15,31–34]

The most hybrid functional applications to solids use the linear combination of atomic orbitals (LCAO) basis set, as is done for molecules. This is explained by the difficulties in the HF method formulation for the PW basis set. Only recently were hybrid functionals implemented in PW VASP (Vienna Ab initio Simulation Package) code for solids.[34] The hybrid XC functionals provide electronic structure of solids in much better agreement with the experiment, in particular for the band gap, usually underestimated in DFT calculations and overestimated in the HF method. However, the question arises of whether there is any need for hybrid functionals in the ground-state calculations, in particular for phonon frequencies. After all, hybrid functionals are at least one order of magnitude more expensive than semilocal GGA functionals. As is stated in Ref. 34, apart from the band gaps (which are not ground-state properties), there are a few other properties that are clearly predicted better by the hybrid functionals. It was found in PW DFT calculations[34] that for Sr(Ba)TiO_3, the ground-state structure of the distorted antiferroelectric phase is in better agreement with experiment, and phonon modes are much more accurate for hybrid XC functionals. The LDA predicts good phonon frequencies if the frequencies are evaluated at the theoretically predicted equilibrium volume because of sizable error compensation (LDA equilibrium volume is too small, but LDA frequencies at the experimental volume are too soft). The GGA drastically underestimates the phonon frequencies as a result of a too large equilibrium volume.

A systematic comparison of DFT and hybrid XC functionals for prototypical ferroelectric oxides $BaTiO_3$ and $PbTiO_3$ was reported in Ref. 33. It was demonstrated that the new hybrid B1-WC (hybrid functional with $B = 1$ and Wu-Cohen DFT exchange) functional allows us to obtain very good structural, electronic, and ferroelectric properties as compared to experimental data for $BaTiO_3$ and $PbTiO_3$. The hybrid B1-WC functional consists of a PBE correlation part and a WC exchange part,[35] which is the modified PBE exchange. The percentage of exact exchange is defined by parameter A, which is varied in calculations with the hybrid B1-WC functional. The best results were found in Ref. 33 for $A = 0.16$. This means that use of the hybrid B1-WC functional introduces an additional parameter in the first-principles calculation. Meanwhile, the hybrid PBE0 functional[30] is parameter-free as the exchange percentage ($A = 0.25$) was found from the perturbation theory. The verdict on which hybrid functional is better for ABO_3 perovskites is still open and requires further theoretical investigations.[34] In the present study, the periodic LCAO approach is applied to calculate the ground-state properties and phonon frequencies for the three crystals Ba(Ti,Zr,Hf)O_3 within the hybrid XC functional PBE0.[30] As mentioned earlier, the hybrid PBE0 functional does not require any adjustable parameters and has been deduced on purely theoretical grounds. This functional has been shown to properly re-produce the properties of many strongly correlated systems (see, for example, Ref. 36).

The outline of the paper is as follows. In Sec. II, we describe the computational details of our calculations. In Sec. III, we report the results obtained for the structural and electronic properties of cubic BTO, BZO, and BHO bulk crystals. The results obtained are compared with the existing experimental data and with those from PW DFT calculations. In Sec. IV, the calculated phonon frequencies at Γ, X, M, and R points of the BZ of a simple cubic lattice are reported. A comparison with the results of other DFT calculations is made. Finally, our conclusions are given in Sec. V.

II. COMPUTATIONAL DETAILS

The cubic perovskite properties and phonon frequencies in the LCAO basis were calculated with CRYSTAL09.[37] The 5s, 5p, and 6s levels of barium, and the ns, np, $(n+1)d$, and $(n+1)s$ levels of the transition metal, were treated as valence states ($n = 3$, 4, and 5 for Ti, Zr, and Hf, respectively).The Gaussian basis set and relativistic small-core pseudopotentials (PP's) of free atoms for Zr and Hf were taken from the PP library of the Stuttgart/Cologne group.[38] The uncontracted Gaussian basis set and small-core pseudopotential for the Ti atom were taken from Ref. 39.

Our approach follows the traditional approach for LCAO calculations, in which pseudopotentials are used to generate atoms using the HF or Dirac-Fock (DF) (for heavy atoms such as Zr and Hf) methods, that is, the atoms are not generated using the hybrid functionals employed in our LCAO calculations. On the other hand, the DFT community working with the PW basis has always favored an alternative approach that involves the generation of corresponding pseudopotentials for each XC functional. It can be argued[31,33] that HF or DF pseudopotentials constitute a reasonable choice in DFT calculations. The pseudopotentials used describe the interaction of core and valence electrons in good agreement with the results of all-electron calculations. This was demonstrated in Ref. 33 for $BaTiO_3$ and $PbTiO_3$ crystals. The values of lattice constants and phonon frequencies obtained from Ti all-electron calculations are very close to those obtained using Ti pseudopotentials. (the largest difference in the lattice constant is 0.006 A, and that in phonon frequencies is $-5\ \mathrm{cm}^{-1}$; see Tables II and VII in Ref. 33).

To avoid spurious interactions between the diffuse functions and the core functions of neighboring atoms,[29] the basis-set diffuse exponents smaller than 0.1 (in Bohr^{-2}) for Ti, Zr, and Hf were removed. The all-electron basis set 8-411G* from Ref. 40 was used for the O atom. This basis set includes polarization d orbitals.

TABLE I. Calculated bulk properties of cubic $BaTiO_3$, $BaZrO_3$, and $BaHfO_3$ crystals. The experimental data are given in parentheses. Q and Z are Mulliken and Born atomic charges, respectively. For Born charges in $BaTiO_3$, experimental data are taken from Refs. 11 and 45. The experimental data are given as cited in Ref. 46.

Property	$BaTiO_3$	$BaZrO_3$	$BaHfO_3$
Cell a (Å)	3.988(3.992)	4.198(4.191[a])	4.193(4.180[b])
Bulk modulus B (GPa)	185(173)	168	171
Cohesive energy E_{at} (eV)	29.9(31.6)	32.9(33.5[c])	33.4
Band gap, E_{gap} (eV)	3.7(3.4)	5.4(5.3[d])	5.9(6.0[e])
Q_{Ba}	1.90	1.87	1.87
Z_{Ba}	2.60(2.9)	2.56	2.55
Q_{Me}	2.24	2.21	2.48
Z_{Me}	7.06(6.7)	5.88	5.56
Q_O	−1.38	−1.36	−1.45
Z_{O1}	−5.64(−4.8)	−4.58	−4.28
Z_{O2}	−2.01(−2.4)	−1.94	−1.91

[a] Ref. 47.
[b] Ref. 50.
[c] Ref. 48.
[d] Ref. 49.
[e] Ref. 20; predicted from the experimental band gap for $SrHfO_3$.

The exponents of noncontracted basis functions were optimized by the method of conjugate directions[41] as implemented in the OPTBAS code.[42] The Monkhorst-Pack scheme for 8 × 8 × 8 k-point mesh in the BZ was applied together with the tolerances 7, 7, 7, 7, and 14 for the one-electron, Coulomb, and exchange integral calculations. These tolerances mean that during direct lattice summations, one-electron and two-electron Coulomb integrals less than 10^{-7} and two-electron exchange integrals less than 10^{-14} are ignored (for details, see Ref. 37).

Furthermore, the forces for the self-consistent cycles were optimized until the energy difference reached 10^{-6} eV for the lattice structure optimization and 10^{-8} eV for the phonon frequency calculations. The calculations of phonon frequencies were based on the following procedure. First, the equilibrium geometry was found by optimizing the cubic lattice parameter a. Second, the phonon frequencies were obtained within the frozen phonon method[43,44] within the harmonic approximation at the optimized equilibrium lattice constant.

A dynamical matrix was calculated for the supercells containing 8, 32, and 64 primitive cells, that is, consisting of 40 160 320 atoms, respectively. The corresponding primitive-cell–supercell transformation matrixes are $\begin{bmatrix} 200 \\ 020 \\ 002 \end{bmatrix}$, $\begin{bmatrix} 22-2 \\ 2-22 \\ -222 \end{bmatrix}$, and $\begin{bmatrix} 400 \\ 040 \\ 004 \end{bmatrix}$, respectively.

All these supercells are compatible with Γ, X, M, and R points of the BZ (at these points, the difference in the three calculated supercell frequencies is not larger than 1–2 cm^{-1}). Two larger supercells are compatible also with k points in the BZ directions: Σ(0.25,0.25,0) and S(0.25,0.25,0.5) for both of them, and Δ(0,0,0.25), T(0.25,0.5,0.5), Λ(0.25,0.25,0.25), and Z(0,0.25,0.5) for the largest supercell.

III. STRUCTURAL AND ELECTRONIC PROPERTIES

Table I presents the results of our calculations for structure parameter (lattice constant a), bulk modulus B, cohesive (atomization) energy E_{at}, electronic band gap E_{gap}, effective charges Q (due to Mulliken population analysis for periodic systems[29]), and Born atomic charges Z. The results are also compared to existing experimental data. As is seen from Table I, use of the hybrid PBE0 XC functional allows us to predict the considered cubic perovskite properties with high accuracy. Mulliken atomic charges Q, given in Table I, demonstrate well-known high covalency in the transition-metal–oxygen interaction. The calculation of atomic Born charges Z was made with the experimental high-frequency dielectric constant $\varepsilon^{\infty} = 5.4$ found for $BaTiO_3$ by extrapolating refractive index measurements at a different wavelength to zero frequency[10] and $\varepsilon^{\infty} = 4.6$ (found in Refs. 20 and 21) for two other crystals. The numerical values of Born charges in $BaTiO_3$ agree with those found in PW DFT calculations[11] and the experimental estimates;[45] see Table I.

IV. PHONON FREQUENCIES

The crystalline phonon mode symmetry is defined by the corresponding space group irreducible representations (irreps) induced from the irreps occupied by the atom site symmetry group corresponding to the atomic displacement (x,y,z).[29,51]

In the cubic perovskite structure, barium and transition-metal atoms occupy Wyckoff positions a and b with the site symmetry group O_h, and an oxygen atom occupies Wyckoff position d with the site symmetry D_{4h}. In the footnote to Table II, the symmetry of phonons is given for the Γ point of the BZ. It is seen that infrared (IR)-active Γ_4^- modes are induced by all five atom displacements, but the silent Γ_5^- mode is induced only by the displacement of three oxygen atoms.[51]

The symmetry of phonons for X, M, and R points of the BZ is given in Table III with the corresponding frequencies. The irreducible representations of the cubic space group $Pm3m$ are labeled according to Miller and Love.[52]

The symmetry of phonons for the nonzero **k** vector is usually given by experimentalists discussing the phonons studied by the neutron-scattering experiments (for example, see

TABLE II. Phonon frequencies (cm^{-1}) at the Γ point of the BZ. 4^-: a (000), t_{1u} (x,y,z); $b(0.5,0.5,0.5)$, t_{1u} (x,y,z); da_{2u} (z), $e_u(x,y)$; 5^-: $de_u(x,y)$; TO: transverse; LO: longitudinal optical phonons.

Phonon	$BaTiO_3$ (this work)	PW LDA (Ref. 9)	PW LDA (Ref. 14)	PW LDA (Ref. 10)	DFPT (Ref. 11)	Expt. (Ref. 53)	$BaZrO_3$ (this work)	PW LDA (Ref. 17)	PW LDA (Ref. 18)	PW GGA (Ref. 19)	Expt. (Ref. 54)	$BaHfO_3$[a] (this work)[a]	PW LDA (Ref. 21)
4^- TO1	281i	178i	151i	195i	177i		129	96	91		115	124	94
4^- TO2	196	177	175	166	112	181	218	193	190	250	210	215	194
5^- silent	314		269	266		306	228		182	250		234	214
4^- TO3	478	468	471	455	534	487	509	513	483	557	505	530	496
4^- LO1	182	173	172	162	111	180	146					134	115
4^- LO2	472	453	439	434	412	468	397					395	214
4^- LO3	677	738	683	657	607	717	677					657	650

[a] Experimental data are absent.

Ref. 44 for LiF crystal). Unfortunately, such publications are unknown for the perovskites under consideration. Therefore, we included in Table III the symmetry classification of the calculated phonons. We hope that future experiments allow a comparison of our data with those found in neutron-scattering experiments.

Phonon frequencies at the Γ point of the BZ are given in Table II in comparison with those found in PW DFT calculations by the linear-response method. It is seen that (i) in agreement with the results of other calculations and experimental observations, the structural instability via soft modes was found only in $BaTiO_3$; (ii) the best agreement between the experimental and calculated frequencies takes place for the present LCAO PBE0 calculations. We explain this both by use of the hybrid XC functional and the optimization of the atomic basis for each of the crystals separately in the framework of the PBE0 XC functional.

The results given in Table III demonstrate that the structural instability in $BaTiO_3$ is connected also with imaginary phonon frequencies at the M and X points of the BZ, but not at the R point. This is in agreement with the results of DFT PW calculations[10,12,14] on phonons in $BaTiO_3$.

The experimentally observed stability of the cubic structure for $BaZrO_3$ and $BaHfO_3$ is in agreement with the results of

TABLE III. Phonon frequencies (cm^{-1}) at the X, M, and R points of the BZ.

k-point, site symmetry	Symmetry	$BaTiO_3$, present work	$BaTiO_3$, Ref. 10, PW LDA	$BaTiO_3$, Ref. 55, PW PBE	Symmetry	$BaZrO_3$	Symmetry	$BaHfO_3$
X (0,0,0.5)	5^-	260i 96i[a]	189i	84i	5^+	95	5^+	99
a (000)	5^+	124	104	109	5^-	132	5^-	103
t_{1u} (x,y,z) 3^-5^-	1^+	161	152	147	1^+	140	1^+	143
	5^-	215	195	204	3^-	230	3^-	179
b (0.5 0.5 0.5)	3^-	285	261	285	5^-	232	5^-	237
t_{1u} (x,y,z) 1^+5^+	4^-	352	323	324	4^-	266	4^-	272
	5^+	360	331	327	5^+	285	5^+	288
d (000.5)	5^-	445	423	439	3^-	466	3^-	433
$a_{2u}(z)$ 1^+5^-	3^-	557	519	518	5^-	492	5^-	516
$e_u(x,y)$ $3^-4^-5^-5^+$	1^+	669	668	630	1^+	735	1^+	745
M(0,0.5,0.5)	3^-	242i, 59i[a]	167i	85i	5^-	94	5^-	94
a (000)	5^-	117	105	111	2^-	94	2^-	98
t_{1u} (x,y,z) 3^-5^-	2^-	125	104	109	3^+	124	3^-	118
	3^+	239	209	194	3^-	154	3^+	128
b (0.5 0.5 0.5)	5^-	302	271	284	5^-	228	5^-	196
t_{1u} (x,y,z) 2^-5^-	3^-	344	334	341	5^+	297	5^+	300
	2^+	357	345	356	5^-	371	5^-	326
d (000.5)	5^+	374	356	364	4^+	431	4^+	435
$a_{2u}(z)$ $1^+2^+3^-$	5^-	464	437	441	3^-	470	3^-	498
$e_u(x,y)$ $3^+4^+5^+5^-$	4^+	494	458	460	2^+	548	2^+	578
	1^+	736	686	722	1^+	789	1^+	796
R (0.5,0.5,0.5)	5^+	148, 134[a]	129	133	4^+	92	4^+	97
a (000) t_{1u} (x,y,z) 4^-	4^+	217	183	167	5^+	114	5^+	118
b (0.5 0.5 0.5) t_{1u} (x,y,z) 5^+	3^+	324	315	389	5^-	318	5^-	226
d (000.5)	4^-	413	388	399	5^+	389	5^+	392
$a_{2u}(z)$ 1^+3^+	5^+	450	416	417	3^+	539	3^+	570
$e_u(x,y)$ 4^+5^+	1^+	772	720	754	1^+	818	1^+	823

[a] Ref. 14.

the present work, as no imaginary frequencies were obtained for these crystals both at the BZ symmetry points (see Table III) and on the six symmetry directions under consideration. We already mentioned that PW DFT calculations[16] on BZO give imaginary phonon frequencies, which contradicts the experimentally observed cubic structure of BZO up to 2 K.

V. CONCLUSIONS

Let us summarize the obtained results.

(i) The first-principles LCAO computations on Ba(Ti,Zr,Hf)O_3 are performed within the hybrid DFT XC functional. We have shown clearly that, with the basis-set optimization and use of the parameter-free hybrid XC PBE0 functional, such calculations are able to predict correctly the structural stability and phonon properties in the cubic perovskites under consideration. In agreement with the experimental data, the structure instability is found for the cubic phase in ferroelectric BTO crystal. For cubic phases of BZO and BHO crystals, imaginary phonon modes are not found, in agreement with their experimentally known stability up to 2 K.

(ii) The symmetry of phonons for the nonzero **k** vector (X, M, and R points of the BZ) is given for each of the calculated phonon frequencies. This will be useful for future comparisons of our results with the experimental data on neutron scattering. At present, there are no such experiments for the three perovskites under consideration.

(iii) The agreement between the experimental and calculated ground-state properties and phonon frequencies is better in the present work than that obtained in DFT calculations. This can be explained both by use of the hybrid PBE0 XC functional and by the optimization of the atomic basis set for each of the crystals separately in the framework of the PBE0 XC functional.

(iv) The results obtained in the present study for $BaHfO_3$ will be very important for future experimental study of the vibrational spectra of this crystal, as such studies have not been performed up to now.

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