

Thermodynamic stability of stoichiometric BiFeO₃ : hybrid DFT study

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Abstract:

BiFeO₃ perovskite attracts great attention due to its multiferroic properties and potential use of Bi_{1-x}Sr_xFeO_{3-δ} and Bi_{1-x}Sr_xFe_{1-y}Co_yO_{3-δ} solid solutions as intermediate temperature cathodes of oxide fuel cells. Similar LaFeO₃ material is a limiting material for well-known highly effective cathode materials (La_{1-x}Sr_xFe_{1-y}Co_yO_{3-δ}) for oxide fuel cells and other electrochemical devices. In this study *ab initio* hybrid functional approach was employed for investigation of thermodynamic stability of both BiFeO₃ and LaFeO₃ with respect to decompositions to binary oxides and to elements as the function of temperature and oxygen pressure. The localized (LCAO) basis sets describing the crystalline electron wave functions were carefully re-optimized within the CRYSTAL09 computer code. The results obtained by considering Fe as all-electron atom and within the effective core potential are compared in detail. Based on our calculations, the phase diagrams were constructed which allow us to predict the stability region of stoichiometric BiFeO₃ in terms of atomic chemical potentials. This permits determining environmental conditions for existence of stable BiFeO₃ and LaFeO₃. These conditions were presented as contour maps of oxygen atoms chemical potential as a function of temperature and partial pressure of oxygen gas. A similar analysis was also performed

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using experimental Gibbs energies of formation. The obtained phase diagram and contour map are compared with the calculated ones.

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1. INTRODUCTION

Both lanthanum and bismuth ferrates are limiting compounds for a set of very efficient cathode materials for solid oxide fuel cells (SOFCs) operating at intermediate temperatures (500-700 °C), while ordinary SOFCs operate at higher temperatures (700-1000 °C).

Lanthanum ferrate LaFeO_3 (LFO) is base for solid solutions $\text{La}_{1-x}\text{Sr}_x\text{Fe}_{1-y}\text{Co}_y\text{O}_{3-\delta}$ which are well-known highly efficient cathodes for SOFCs¹. Bismuth ferrate BiFeO_3 (BFO) is base for the perovskite solid solutions $\text{Bi}_{1-x}\text{Sr}_x\text{FeO}_{3-\delta}$ and $\text{Bi}_{1-x}\text{Sr}_x\text{Fe}_{1-y}\text{Co}_y\text{O}_{3-\delta}$, which were recently also proposed as promising cathodes for SOFCs.²⁻⁵ In the same time BFO continues to attract considerable attention due to its multiferroic properties⁶ at ambient conditions. It has also been found that photocatalytic⁷ and photovoltaic⁸ properties of BFO are enhanced due to its ferroelectricity.

Independently from area of application, understanding the thermodynamic stability of LFO and BFO is vital to provide a foundation for future investigations of the formation of intrinsic defects, surface structures, solid solutions, and surface chemical reactions (e.g. oxygen reduction reaction), as well as formation of solid solutions, like the mentioned above cathode materials, their possible structures and stability. The stability behavior also provides valuable guidance to the appropriate conditions to be used when synthesizing these materials.

Exploration of formation energies of LFO was performed in many experimental studies⁹⁻¹⁴ using various calorimetric and electrochemical techniques. However, spread of Gibbs free energy of formation of LFO from La_2O_3 and Fe_2O_3 oxides obtained in different experiments is very large: from¹³ 23 kJ/mol to 92 kJ/mol.¹⁴ Such a difference come out of various electrochemical experiments. It appears to be due to neglect of formation of oxygen vacancies at high temperatures and polarization of electrodes.¹⁰ Only one measurement of

the energies of formation BFO has been attempted to our knowledge. It was performed using solution calorimetry and calvet calorimetric measurements.¹⁵

Estimates of the energy (enthalpy) of formation for LaBO_3 (where B stands for fourth-period transition metals here, sitting in respective B-site of ABO_3 perovskite structure) has been calculated using generalized gradient approximation¹⁶ (GGA) within density functional theory (DFT) and DFT+ U technique¹⁷, where on-site Hubbard U -correction for intra-atomic Coulomb interactions is applied. Following to analysis¹⁸ performed for oxides, this works applied correction to the energies of formation on overbinding in O_2 in DFT calculations. A dependence on electron correlation (self-interaction) in transition metal can be accounted¹⁸ by choosing appropriate for each metal Hubbard U parameter. Such approach was employed to study oxygen vacancy formation energetics in the bulk^{17,19} and at (001) BO_2 -terminated surfaces¹⁷ as well as O adsorption at the same surfaces¹⁷. Hybrid density functionals (hDF), wherein DFT exchange functionals are mixed with precise non-local Fock exchange terms, were recently used for modeling of oxygen vacancies and protonic defects formation in LaFeO_3 and $\text{La}_{1-x}\text{Sr}_x\text{FeO}_3$ solid solutions²⁰⁻²².

Several relevant theoretical studies of BFO have been performed within the last few years. In particular, the relative stability of various charged defects was considered in refs. 23, 24, and the formation enthalpy of defect-free BFO is analyzed in ref. 25, aimed at optimizing conditions for BFO thin film growth. The local density approximation (LDA) with on-site Hubbard U -correction (LDA+ U) was applied in these calculations in order to estimate BFO formation enthalpy, with a focus on BFO formation from binary oxides Bi_2O_3 and Fe_2O_3 . However, it is well-known that all DFT+ U approaches have difficulties for simultaneous modeling materials (especially oxides) containing transition metals or f -elements having different degrees of the metal oxidation. One of reasons is that the effective one-center Coulomb interaction parameter U_{eff} depends on the oxidation state of the transition or f -metals is well described by a single Hubbard- U parameter. This problem could be avoided by using hDF. Such hDFs have been shown to yield substantially better results for the atomic and electronic structure (including band gaps) of transition metal oxides²⁶⁻²⁸ than other approaches do. In addition, such hDFs treat anions and ordinary (e.g. Ba, Sr) metal ions in the same way as transition and f -metal ions, while in DFT+ U the one-site Coulomb correction is applied usually to the latter ions only. Also, hDFs

produce pretty good the binding energy in O_2 ;²⁹ therefore, there is no need for the correction of the energies of formation on the overbinding.

Here we present the results of ab initio calculations using hDFs on all LFO, BFO and the products of their decomposition – lanthanum oxide La_2O_3 , bismuth oxide Bi_2O_3 and Fe oxides (FeO , Fe_2O_3 , and Fe_3O_4) in various phases – and we determine the range of possible chemical potentials for all involved elements (La, Bi, Fe and O) within which LFO or BFO can exist. These data are used for the thermodynamic stability analysis allowing us to predict the LFO and BFO stability regions as a functions of temperature and oxygen pressure. In the next Section 2 details of employed theoretical approach are described. The results of ab initio calculations and LFO and BFO stability analyses are described and discussed in Section 3. Summary of the performed study and conclusions are given in the last Section 4.

2. THEORETICAL

A. Computational details

Ab initio calculations were performed using the CRYSTAL09 computer code³⁰ with the localized atomic (Gaussian-type) basis functions centered at atomic nuclei and applied to expand one-electron orbitals (linear combination of atomic orbitals). The B3PW³⁰⁻³⁵ hDF was employed, which includes a “hybrid” (mixture) of nonlocal exact Fock’s exchange, gradient-corrected (used in GGA), and LDA exchange potentials combined with the GGA correlation potential of Perdew and Wang. The presence of Fe ions in materials under study suggests the presence of electron correlation effects. The use of the hDF in modelling Fe-containing materials considerable reduces self-interaction errors of the standard density functionals. As it was mentioned above, employing hDF allows to avoid a need in correcting the formation energies on overbinding in O_2 molecules.

A series of Coulomb and exchange integrals were truncated using overlap thresholds of 10^{-8} , 10^{-8} , 10^{-8} , 10^{-8} , and 10^{-16} .³⁶ The Monkhorst–Pack grid for integration over the Brillouin zone in the reciprocal space was chosen to ensure that distances between neighbor points of the net are smaller than 0.18 \AA^{-1} for materials and unit cells under study. The self-consistent calculations were continued until the total energy changes decreased below 10^{-8}

Hartree. The atomic structures were optimized completely (both unit cell parameters and internal atomic positions), until simultaneously the following four conditions were fulfilled: the largest absolute (la) value and the root mean square (rms) values of atomic forces are smaller than 4.5×10^{-4} and 3.0×10^{-4} a.u., and the la and rms values of the atomic displacements smaller than 1.8×10^{-3} and 1.2×10^{-3} a.u., respectively.

B. Effective Core Potentials

In order to save computational time, the inner core electrons of heavy atoms were replaced by effective core potentials (ECPs) (or pseudopotentials). The latter mimic potentials of the replaced core electrons interacting with the rest of electrons in the system. The scalar-relativistic energy-consistent ECPs from the Stuttgart/Cologne group³⁷ were used in this paper. Electrons of two external (valence and core-valence) electron shells were not included into the ECPs but described explicitly. Therefore, the ECP46MWB³⁸⁻⁴⁰ and ECP60MFD^{41,42} potentials were used for heavy La and Bi atoms. In contrast, O atoms have only two electron shells (with main quantum numbers $n=0, 1$), thus all electrons at O atoms were described explicitly (all-electron basis set). Computational time saved by using ECPs at Fe atoms is moderate because only 10 electrons occupy two inner core shells with main quantum numbers $n=0,1$. (Therefore, before starting calculations, one has to evaluate savings due to the use of the ECP). Here we performed our modelling for both cases: (i) ECP10MFD^{43,44} at Fe atoms and (ii) all-electron Fe ion treatment, in order to decide upon the best choice for further simulations.

C. Basis sets optimization

The essential element of the LCAO calculations is a choice of the atomic basis sets. Some recommended basis sets are available at the CRYSTAL code homepage⁴⁵, but no small-core basis set was available so far for Bi. We also needed a consistent basis set for all elements, involved in Thus, we performed the basis set optimization employing our own computer code^{46,47}. It was designed as the external utility driving the basis set optimization through minimization of the total energy. This code creates the input for the CRYSTAL09, call it for execution, reads necessary information from output file and determines the next set of

parameters for which the CRYSTAL09 has to be run at the next step, according the conjugated gradient optimization method. The optimization was performed until the forth significant digit of each optimized basis set parameter had converged.

In our previous CRYSTAL studies^{46,47}, the oxygen basis set was based on “O_8-411_muscat_1999” or “O_8-411_towler_1994” basis sets⁴⁵. Then two uncontracted *d*-orbitals were added and all split *s*-, *sp*- and *d*- Gaussian basis functions were re-optimized, in order to minimize the total energy. However, in the beginning of the present study we performed additional tests which indicated that all basis functions noticeably change during optimization when allowed. Therefore, the basis set was re-optimized completely. Our previous experience suggested that it is sufficient to optimize *s*- and *sp*-orbitals in the O₂ molecule and that further optimization in an oxide crystal does not produce any significant changes and improvements. However, if only a single *d*-orbital is included to the oxygen basis set, then the parameter α defining diffusivity of this Gaussian function strongly depends on surrounding atoms. If the oxygen basis set was optimized in the free O₂ molecule, the *d*-orbital becomes less diffuse than in a crystal. Also, the *d*-orbital had to be optimized in the O₂ molecule, to reproduce the experimental bond length and the dissociation (binding) energy. These values need to be evaluated accurately enough in the simulations such as the present one, where the results strongly depend on the correct calculation of the energies of formation for various oxides. To ensure a good description of both free molecule and oxide crystals, we used two *d*-functions in the oxygen basis set, where a more contracted *d*-function was optimized in the O₂ molecule whereas another, more diffuse *d*-orbital was optimized in an oxide crystal. A similar approach was adapted in the present work. The oxygen basis set was built according to the s8sp411d11 contraction scheme (8 contracted together *s*-Gaussian type functions, 3 *sp*-basis functions, where the first of which contains 4 Gaussians, while other two *sp*-functions contain a single Gaussian function each, and two uncontracted *d*-functions the Gaussian-type functions with the same exponential parameters are used in *sp*-functions for expression of the corresponding basis function). All basis functions except the most diffuse *d*-function were optimized in the O₂ molecule with the experimental bond length of 1.21 Å.⁴⁸ The most diffuse *d*-function was taken from the basis set⁴⁶ and then re-optimized in SrO crystal. The basis set for Sr was optimized with the original polarization *d*-orbital (more diffuse of two

d-basis functions) before the latter was re-optimized in its turn. Similarly, 28 inner electrons on Sr ion were replaced by the ECP28MDF^{49,50} pseudopotential, while the remaining electrons were described explicitly, using the basis set with s411p411d11 contraction scheme. The optimization of the basis set for Sr ion was done for the experimental face centered cubic (fcc) SrO crystal structure⁵¹ with the lattice constant $a_0=5.198 \text{ \AA}$. During the following re-optimization of the polarization (diffuse) d -function on the O-atom, it did not change. Therefore, there was no need for further adjustment of the basis set on Sr ion.

Both all-electron and pseudopotential basis sets for Fe atoms were optimized for the FeO crystal, where the O atom was treated with the newly optimized basis set. At ambient conditions, FeO has the fcc structure⁵² (space group $Fm\bar{3}m$, #225) with the lattice constant $a_0= 4.332 \text{ \AA}$. For the Fe ion basis set optimization, this structure was slightly compressed along the [111] direction⁵³, to ensure splitting between d -orbitals at Fe ions and reliable convergence of the electronic structure calculations. These calculations were done for the ferromagnetic spin order what allows us to use the smallest possible unit cell of FeO containing only two atoms. The all-electron basis set for Fe was produced according to the s86411p6411d411 contraction scheme. For calculations employing ECP, 10 core electrons were replaced with the ECP10MFD^{43,44} pseudopotential and the rest of electrons were described using the basis set with s411p411d411 structure.

Optimization of basis sets for La and Bi atoms was performed using LaAlO₃ and BiAlO₃ compounds taken in cubic perovskite structures corresponding⁵⁴ to high-temperature phase of LaAlO₃ with its experimental lattice constant 3.81 \AA . Such choice was made because both La and Bi atoms are surrounded by environment very similar to the one which we are studying, which has the same symmetry (group $Pm\bar{3}m$, #221). Also, the Bi oxide Bi₂O₃ contains 20 atoms in unit cell and has relatively low symmetry, which greatly complicates its direct use in the basis set optimization. And lastly, ionic radii of La³⁺ and Bi³⁺ ions are very close. Despite the fact that BiAlO₃ crystal is, unlike LaAlO₃, thermodynamically unstable, it was sufficient for the Bi atom basis set optimization and for representing its position in a similar perovskite type crystal. The quality of these optimized

basis sets is checked below in Section 3 for the calculations of basic properties of the two different phases of La_2O_3 and Bi_2O_3 .

The internal 46 electrons at La atoms were replaced by ECP. As it is usual for La ions, it is important to examine effects of f-orbitals. Therefore, two valence basis sets were optimized and then employed in this work: (i) the one with s4411p411d411 contraction scheme and (ii) another with s4411p411d411f11 contraction scheme, where two separate f-orbitals were added to the basis set.

The ECP replaced 68 of Bi ion core electrons whereas the valence and core-valence electrons were represented using the basis set for s4411p411d411 contraction scheme. An additional s-basis function was introduced because in the Bi^{3+} ion s-orbital of the outer valence atomic shell is occupied by two electrons, while in many other ions such as in the above mentioned Sr^{2+} , Al^{3+} , Fe^{3+} , or La^{3+} the outer valence atomic shell usually is only slightly occupied in crystals.

Electrons on Al atoms are described using the all-electron basis set with s8511p511d11 contraction structure.

At the first step basis sets for La (without f-orbitals) and Al were optimized in LaAlO_3 simultaneously. We used basis set for O optimized earlier in this work. Then, we added two uncontracted f-orbitals to La and re-optimized all orbitals at La atom, keeping obtained basis set for Al the same. Following attempt to further optimize basis set at Al, while using basis set of La with f-orbitals, showed that the basis set at Al is stable and does not change. Finally, basis set at Bi atoms was optimized in BiAlO_3 , where basis sets at Al and O had been already obtained.

The optimized basis sets for all mentioned elements (O, Al, La, Bi, Fe, and Sr) are provided in Supplementary material⁵⁵ (Tables S1-S7) and could be also found at CRYSTAL's website.⁴⁵

D. Thermodynamic analysis of material stability

The stability region of ABO_3 perovskite could be estimated by comparing the Gibbs free energies of the perovskite crystal with those of the binary oxides and elemental A and B metals (in this study $A=\text{La}$ or Bi , $B=\text{Fe}$). The pV term in the Gibbs free energy of solids is

very small and thus is traditionally neglected. The vibrational (phonon) contribution to the Gibbs free energy of crystals usually depends very weakly on temperature due to nearly complete cancelation of changes in the vibrational contributions to the internal energy and to the entropy term TS .⁵⁶ Therefore, we also neglected the phonon contribution to the Gibbs free energy. This approximation allows us to replace the Gibbs energies (per formula unit) g for solids by the total electron energies E obtained in the standard electronic structure calculations, $g \approx E$. To express the Gibbs free energies of metals, we use deviation of chemical potentials of the metals M from their values in the standard states the latter coincide with the Gibbs energies of an atom in respective metals:

$$\Delta\mu_M = \mu_M - g_M^{bulk} \approx \mu_M - E_M . \quad (1)$$

The variation of the O atom chemical potential is defined with respect to the O atom energy in a free O₂ molecule:

$$\Delta\mu_o(T, p_{O_2}) = \mu_o(T, p_{O_2}) - \frac{1}{2} E_{O_2} , \quad (2)$$

where T is the temperature and p_{O_2} oxygen gas partial pressure. The ideal gas model can be used for oxygen gas³⁶:

$$\Delta\mu_o(T, p_{O_2}) = \frac{1}{2} \left\{ \Delta G_{O_2}^{gas}(T, p^0) + k_B T \ln\left(\frac{p_{O_2}}{p^0}\right) \right\} + \delta\mu_o^0 . \quad (3)$$

Here $p^0=1$ atm. is the standard pressure, k_B Boltzmann constant, the first term in brackets is the temperature change of the oxygen Gibbs free energy at the standard pressure, and the correction $\delta\mu_o^0$ is chosen as to match the origin of the experimental variation of the O chemical potential and the reference point in our theoretical estimates ($E_{O_2}/2$).

$\Delta G_{O_2}^{gas}(T, p^0)$ could be taken either directly from the experiments, or estimated theoretically, using the ideal gas model and representation of the O₂ molecule as a rigid dumbbell, e.g. ref. 57. The experimental data from NIST Chemistry WebBook⁴⁸ were used in this paper. As a consequence of neglecting the temperature dependence of the Gibbs energy for solids (due to neglecting vibrational contributions), it is only the oxygen chemical potential, for which the temperature dependence and oxygen gas partial pressure

are explicitly taken into consideration. Therefore, the temperature dependence of the Gibbs energies of formation is determined here entirely by the chemical potential of O₂ gas.

In ABO_3 the chemical potentials of three elements involved are connected by the relation

$$\mu_A + \mu_B + 3\mu_O = g_{ABO_3} \approx E_{ABO_3} \quad (4)$$

Using definitions (1) and (2), this can be replaced by the equivalent relation

$$\Delta\mu_A + \Delta\mu_B + 3\Delta\mu_O \approx \Delta E_{f,ABO_3} \quad (5)$$

Hereafter the energies of formation ΔE_f for a compound $A_aB_bO_c$ (any of stoichiometric coefficients a or b can be equal to 0, to include simple oxides to this definition) are

$$\Delta E_{f,A_aB_bO_c} = E_{A_aB_bO_c} - aE_A - bE_B - \frac{c}{2}E_{O_2} \quad (6)$$

where E_A is the energy of atom A in metal A , $E_{A_aB_bO_c}$ is the total energy of the compound $A_aB_bO_c$ (per unit cell). According to Eq. (5), only two of three chemical potential variations are independent variables. $\Delta\mu_O$ has to be chosen as one of these independent variables, in order to relate the results of our analysis with the environmental conditions; $\Delta\mu_{Fe}$ is used here as the second independent variable.

Using the approximation $g \approx E$, definitions of the chemical potential variations, Eqs. (1) and (2) together with Eq.(5), the range of the chemical potentials within which ABO_3 is stable and formation of other materials is prevented, could be formulated as follows. The variation of the O atom chemical potential cannot be positive

$$\Delta\mu_O \leq 0 \quad (7)$$

whereas formation of a pure metallic A or B is prevented, provided

$$\Delta\mu_B \leq 0 \quad (8)$$

and

$$\Delta\mu_B + 3\Delta\mu_O \geq \Delta E_{f,ABO_3} \quad (9)$$

formation of iron oxides is avoided, provided

$$x\Delta\mu_B + y\Delta\mu_O \leq \Delta E_{f,B_xO_y} \quad (10)$$

whereas growth of A_2O_3 oxide cannot occur, provided

$$2\Delta\mu_B + 3\Delta\mu_O \geq 2\Delta E_{f,ABO_3} - \Delta E_{f,A_2O_3}. \quad (11)$$

Usually hDFs, as the B3PW used in this study, provide very good description of molecules and non-metallic materials, but energies, unit cell dimensions and atomic positions obtained for metals are not very reliable. In calculations with local basis sets even more uncertainty is introduced because calculations of metals demand adding more diffuse basis functions, which could be very difficult to optimize in metals. Also, calculations performed with different basis sets are not consistent and difficult to compare or to use in the same simulations. Therefore, another approach was applied here avoiding need for calculations of metals. Instead, this approach requires use of experimental values of the oxide energies of formation. The same approach was earlier applied for a similar investigation of LaMnO_3 stability.⁵⁸

Usually, several oxides exist for a given metal. In the case of LFO and BFO only one stable oxide (La_2O_3 and Bi_2O_3) exists for each La and Bi metals, but three different oxides (FeO , Fe_2O_3 , Fe_3O_4) for Fe. Energies of the metals in their standard states E_M could be obtained using the definition of the Gibbs energies of formation for the binary oxides M_xO_y ^{56,57}

$$E_M = \frac{1}{x} (E_{M_xO_y} - \Delta G_{f,M_xO_y}^0 - \frac{y}{2} (E_{O_2} + \Delta G_{O_2}^{gas}(T^0, p^0) + \delta\mu_O^0)), \quad (12)$$

where $\Delta G_{f,M_xO_y}^0$ is the Gibbs energy of formation for oxide M_xO_y under the standard conditions available from thermodynamic tables⁵⁶, $E_{M_xO_y}$ total energy of M_xO_y oxide (per unit cell) and $\Delta G_{O_2}^{gas}(T^0, p^0)$ change of the Gibbs energy of oxygen gas from 0 K to the standard conditions. The metal energies obtained from several different oxides (e.g. for Fe atom from three oxides) are then averaged to get a common reference.

Using the above defined energies of formation (6) and the variation of the O atom chemical potential, the Gibbs energies of formation for compound $A_aB_bO_c$ can be expressed as

$$\Delta G_{f, A_a B_b O_c}(T, p_{O_2}) = E_{A_a B_b O_c} - aE_A - bE_B - c\mu_o(T, p_{O_2}) = \Delta E_{f, A_a B_b O_c} - c\Delta\mu_o(T, p_{O_2}). \quad (13)$$

This illustrates also meaning of the energies of formation (6) as the Gibbs energies of formation at T=0K.

3. RESULTS AND DISCUSSION

A. Structure and relative energies for various related materials

As the first step, the basic properties of the equilibrium atomic structure for several phases of Bi and Fe oxides and BFO were calculated and compared with available experimental data. Several magnetic states of iron oxides were considered, in order to determine the state lowest in energy. The B3PW hybrid functional gives for the free O₂ molecule (used in our calculations as the reference state) a bond length of 1.202 Å and a binding energy of 5.38 eV that agree well with the experimental values of 1.208 Å and 5.12 eV.⁴⁸

At ambient temperatures spins of Fe atoms in both LFO and BFO have anti-ferromagnetic (AFM) ordering. There are three possible AFM phases in a perovskite lattice: (i) in the A-type AFM the Fe ion spins have ferromagnetic (parallel) ordering within the (001) planes, but spins in nearest neighboring planes are oriented oppositely (ii) in the C-type AFM order spins are ferromagnetically ordered along one of the [001] directions, but AFM-ordered (anti-parallel) in the planes perpendicular to this direction and (iii) in the G-type AFM case spins of all nearest neighbor iron ions are oppositely directed. The later ordering is the most stable one in the both considered here perovskites.^{59,60}

The observed structure of LFO crystal is orthorhombic and belongs to *Pnma* space group (#62) converting to the cubic perovskite structure at high temperature (T= 1253 K). Since the low temperature orthorhombic structure of LFO contains 4 perovskite unit cells. The cubic extended (2x2x2) cell was used in the calculations for the cubic phase of LFO. This cell allows to model easily all magnetic structures possible in perovskite lattice. The complete set of results of LFO calculations is provided in Supplementary material⁵⁵ (Table S8). It includes lattice parameters and relative energies (per the smallest perovskite unit cell from 5 atoms) calculated for both structural phases of LFO, for all 4 magnetic orders,

and performed using all combinations of basis sets at Fe and La. A shortened version of this results is given in Table I, where results for FM and AFM (G) magnetic orders are shown. The lowest in the total energy magnetic order in both phases and for all employed basis sets is AFM (G) in agreement with experimental data.^{59,61} The next in the energy is AFM (C) magnetic state. The AFM (A) follows. And FM state is the highest. All calculated lattice constants pretty well reproduce their experimental values for both phases. The obtained lattice constants are overestimated by less than 1%. Introduction of more approximations to the calculations (ECP at Fe atoms or omission of f-orbitals in the basis set at La) leads to a very small expansion of the unit cells. The optimized internal coordinates in the orthorhombic lattice of LFO for AFM (G) magnetic order are compared with experimental data in Table II. In all calculations obtained coordinates are nearly coincide with experimental values.

Under ambient conditions, BFO has the ferroelectric (FE) perovskite structure⁶², similar to a common ferroelectric LiNbO_3 (the symmetry space group $R3c$, #161) its rhombohedral unit cell contains two formula units (10 atoms). In turn, we used the same cell from 8 formula units ($2 \times 2 \times 2$ extended unit cell) to model the cubic BFO as it was done for cubic LFO.

In the cubic BFO perovskite structure, both FM and possible AFM orders were modeled whereas for the FE structure only FM and the G-type AFM spin orders were considered. The main results are presented in Table 3. In agreement with experiments, AFM (G) spin order is the most stable configuration for both FE and cubic BFO. The experimental atomic structure of the lowest in energy FE (the space group $R3c$, #161) state with AFM (G) spin order is very well reproduced in the present calculations: the largest deviation between calculated vs. experimental lattice parameters is only 0.9%. The cubic structure is by $\sim 1\text{eV}$ higher than the FE one. The FM state is the highest in energy. The AFM C-type state is lower in the total energy than the A-type state. The calculated and experimental atomic positions within FE unit cell of BFO are compared in Table 4. The optimized atomic coordinates are in a very good agreement with the results of measurements⁶² for both Fe ion basis sets.

The atomic structures of the two most stable experimentally observed phases of each La_2O_3 and Bi_2O_3 were optimized and are presented in Tables V and VI. These oxides are not magnetic.

The most stable phase of La_2O_3 is cubic belonging to $Ia\bar{3}$ space group (#206) with the next one being trigonal with space group $P\bar{3}m1$ (#164). The same result is obtained in the present calculations. The lattice constant of the cubic phase is only by 0.5% larger than the experimental one, if f-orbitals are present in the basis set for La. Exclusion of these orbitals from the basis set causes increase of the lattice constant by another percent over the experimental value⁶³. Similarly, in calculations of the trigonal phase the excess over experimental results^{63,64} of the lattice constants is within 0.5% if the basis set includes f-orbitals and about a percent more, when these orbitals are omitted.

In agreement with experimental observations⁶⁵⁻⁶⁷, monoclinic phase with $P2_1/c$, #14 symmetry group has the lowest energy. Two lattice parameters \mathbf{a} and \mathbf{b} are slightly overestimated, while the third one is slightly underestimated. The largest deviation occurs only for the parameter \mathbf{a} (2%), while two other lattice parameters deviate from the experimental values by less than 1%. In the tetragonal β -phase of Bi_2O_3 (symmetry group $P\bar{4}2_1/c$, #114) the lattice parameter $a(=b)$ is more overestimated, by 4% whereas \mathbf{c} parameter is overestimated only by 1.35%.

Under ambient temperatures FeO has the rock salt lattice structure (face-centered cubic, fcc) in the absence of spin ordering, it belongs to $Fm\bar{3}m$ (#225 symmetry group).⁵² Below the Neel's temperature $T_N=198$ K, spins on Fe atoms acquire anti-ferromagnetic (AFM) order with a spin alteration along the [111] direction. Correspondingly, the crystal symmetry becomes reduced to $R\bar{3}$ group (#148). The results of our (TABLE VII**Error! Reference source not found.**) are in good agreement with experiments. The state with the lowest energy, indeed, has AFM order with spins that alternate in the [111] direction. The FM states have higher energies than the AFM state of the same symmetry. The AFM state with alternating spins along the [001] direction has larger energy than the FM state with the rhombohedral symmetry. The lattice constant in the lowest energy state (AFM with opposite spin orientations in the neighbor (111) planes) for the electronic structure calculations. The final lattice parameters are in very good agreement with the is

underestimated by 1.6% in comparison with experiment. The cubic lattice is slightly compressed along the cube diagonal, in contrast to the experimentally determined structure, where the lattice is slightly stretched in this direction. Since under the standard conditions FeO has the fcc lattice, it was necessary to recalculate the lowest in energy AFM state at this geometry. To do this, the symmetry of the lowest state was kept while angles between axes were pulled back to 90° within several steps of optimizing lattice spacing manually. At each step, the density matrix from a previous step was used as the initial guess for iterative procedure experiment (TABLE VII). The obtained total energy of the lowest state for the fcc lattice is only by ≈ 12 meV/f.u. higher than in the fully optimized crystal structure. The total energy of this state obtained for fcc lattice was used later for constructing the BFO phase diagram.

There are four known Fe_2O_3 phases, and by convention they are labelled from α to ϵ .⁶⁸ However, Fe_2O_3 in γ - phase has a large number of randomly distributed cation vacancies, and modelling such a material requires complicated and much more expensive techniques than just standard electron structure calculations. On the other hand, the calculations of this phase do not contribute to the phase diagram of BFO and analysis of its stability because the present approach uses only a single representative structural phase which usually is the most stable one under the standard conditions. Therefore, we did not calculate the γ -phase in the present study. Similarly, because β - and ϵ -phases contain many magnetic Fe atoms in their unit cells with a large number of possible spin orders, and since also their magnetic structures are not well known, only the FM spin ordering was considered for these two phases. The most extensive consideration was given to the α -phase, the most stable and thus most relevant for our study.

The results of calculations for Fe_2O_3 are summarized in TABLE VIII. The experimentally observed sequence of the three considered Fe_2O_3 phases is well reproduced in our calculations. The α -phase with AFM spin ordering has the lowest energy, in agreement with experiment. This phase has the same hexagonal crystalline lattice as corundum ($\alpha\text{-Al}_2\text{O}_3$). (Note that the calculated energy of α -phase with FM order is higher than that for β -phase with FM order.) Lastly, the ϵ -phase has the highest energy among three considered. The lattice constants of Fe_2O_3 in α -phase with AFM order exceed the experimental ones by less than 0.5%, for β -phase the error is larger, 0.8%, and reaches 2.5% in ϵ -phase.

Finally, iron oxide Fe_3O_4 at $T > 120\text{K}$ has the cubic inverse spinel structure with the symmetry corresponding to the $Fd3m$ (#227) group. This phase has a ferri-magnetic (FiM) spin ordering, where Fe ion spins at two tetrahedral sites in the elementary unit cell have the same direction, while those in four octahedral sites have the opposite direction. Upon cooling below $T_V \approx 120\text{K}$, Fe_3O_4 undergoes the Verwey phase transition,^{70,71} which is supposedly associated with a localization of electron charge on two of four Fe atoms in octahedral sites, resulting in their formal charges $+2e$ while another pair of Fe atoms in octahedral sites retaining formal charges $+3e$. Simultaneously, the crystalline lattice is slightly compressed along the chains of Fe atoms with formal charges $+2e$ and elongates along the chains of Fe atoms in the octahedral sites with charges $+3e$. Formal charges of Fe atoms in tetrahedral sites are $+3e$ and did not change during Verwey phase transition. This charge ordering suggests reduction of the lattice symmetry from cubic to orthorhombic.

However, the real structure of this phase is still subject of investigation. According to x-ray and neutron diffraction experiments performed on powders (see ref. 72 and discussions in it), there is also a monoclinic distortion of the lattice. These experiments suggest a doubling of unit cell of the spinel along the [001] crystallographic direction. Theoretical investigation of this distorted structure continues⁷³⁻⁷⁵, but still remains controversial. Note that the purpose of this study is not investigation of the structure of this oxide, but calculation of BFO stability region. Therefore, we applied a simplified model, using just a regular spinel unit cell without doubling it. All possible magnetic orders were tested, to find out which order shows the lowest total energy.

The lattice parameters and relative energies of several low-in-energy magnetic configurations are presented in TABLE IX. The magnetic configuration of the state with the lowest energy reveals the same ferrimagnetic ordering as that observed at temperatures above the Verwey transition: spins on Fe atoms in tetrahedral and octahedral sites are oppositely directed. However, the optimized crystalline structure of this lowest-energy state shows the orthorhombic symmetry (space group $Fddd$, #70). Deviations of the calculated lattice constants from the experimental ones lie within 1.5%. The Mulliken atomic charges on Fe atoms in tetrahedral sites are $+1.98 e$ (all-electron calculations) or $+1.86 e$ (ECP calculations). In its turn, the charges on Fe atoms in two types of octahedral sites are $+1.64 e$ and $+1.96 e$ (all-electron calculations) or $+1.55 e$ and $+1.87 e$ (ECP

calculations), respectively. The relevant magnetic spins on the Fe atoms calculated by means of the Mulliken population analysis are $4.10 \mu_B$ (Fe atoms in tetragonal sites), $3.72 \mu_B$ and $4.20 \mu_B$ (Fe atoms in octahedral sites) in all-electron calculations in the ECP calculations the Fe atoms have magnetic moments of $4.18 \mu_B$, and $3.76 \mu_B / 4.28 \mu_B$, respectively. This is qualitatively consistent with the expected value for the mechanism of the phase transition proposed originally by Verwey himself^{70,71} Fe formal charges +2e, +3e and magnetic moment projections $4 \mu_B$ and $5 \mu_B$, respectively. However, the difference of the charges in the octahedral sites is just $\sim 0.3e$ and in spins $\sim 0.5 \mu_B$ probably due to the considerable covalence of the Fe-O chemical bonding.

There are several close in energy magnetic configurations which reveal the AFM ordering within the chains of Fe^{2+} ions (TABLE IX). The crystalline lattice symmetry in these states becomes monoclinic (space group $P2/m$, #10). This suggests another possible explanation for the monoclinic structure of Fe_3O_4 below the Verwey transition that is based on flipping of spins in one of chains of Fe atoms in octahedral sites, in contrast to the “tri-polaron” model, refs. 72-74. Still, the present simulations are insufficient to make final conclusions about the crystalline structure, and thus further investigations are necessary.

Since under standard conditions Fe_3O_4 instead of low-temperature monoclinic (or orthorhombic) structure is cubic, two crystalline structures were additionally considered. One of these was the usual cubic spinel structure (space group $Fd\bar{3}m$, #227) supposedly observed under the standard conditions. The optimized lattice constants in this structure for both Fe basis sets exceed the experimental values by less than 0.3% and the total energies per Fe_3O_4 f.u. exceed those for a fully optimized structure, by $0.52 eV$ in calculations with ECP and core-valence basis set on Fe atoms and by $0.39 eV$ in all-electron calculations. Another structure is the rhombohedrally distorted spinel lattice (space group $R\bar{3}m$, #166). In such a structure, one of octahedrally coordinated Fe atoms retains the charge +3e and the two electrons are spread over the remaining three Fe atoms in octahedral sites. This structure corresponds to a barrier configuration for the switching direction of the orthorhombic distortion in the cubic spinel lattice mentioned above. If Fe_3O_4 crystal were heated at high enough temperature to overcome this barrier, the localized electrons will continuously jump from one pair of iron ions in octahedral sites to another. In other words, these electrons will delocalize over all Fe atoms in octahedral sites. This

corresponds to the phase transition from the low-temperature phase to the cubic higher-temperature one (space group $Fd\bar{3}m$, #227). The energy of such a state can be estimated by the barrier configuration as 0.18 eV for the ECP and 0.12 eV for the all-electron basis set above the energy of fully relaxed orthorhombic unit cell (space group $Fddd$, #70). That is, in this study the total energy of the barrier structure corresponds to the energy of Fe_3O_4 crystal in the higher-energy state, which is stable under standard conditions it will be used below to construct the BFO phase diagram.

Overall, good agreement between the experimental and optimized structures for La_2O_3 , Bi_2O_3 and iron oxides demonstrates the sufficiently high quality of the optimized basis sets.

B. Stability regions

Eq. (12) was used to obtain the reference energies of La, Bi and Fe metals. In these calculations, cubic AFM structures of FeO and the barrier rhombohedral structure of Fe_3O_4 are used because these structures represent the most stable ones under standard external conditions. For all other materials the most energetically stable phases were also employed. Eq. (6) was then used to calculate the energies of formation for all relevant oxides, LFO and BFO. As was mentioned before, these energies of formation represent the Gibbs free energies of formation for materials at $T=0\text{K}$. All calculated energies are summarized in TABLE X and were used to build the phase diagrams (Figs. 1-4) necessary for the analysis of LFO and BFO stability. The obtained energies for La, Bi and Fe metals were also used to obtain the standard Gibbs energies of formation, Eq. (13), for La, Bi and Fe oxides and for LFO and BFO perovskites. The calculated Gibbs energies of formation for iron oxides allow us to estimate the quality of employed hybrid functional and the procedure used for calculating the energies of formation.

1. Iron oxides.

The largest discrepancy between calculated and experimental standard Gibbs energies of formation is for FeO (5.9% for calculations with ECP and 7.6% for all-electron calculations). However, the absolute error in the calculated standard FeO Gibbs energy of formation is even smaller than for Fe_3O_4 . This occurs because the Gibbs energy of formation for FeO is,

approximately by a factor of three, smaller than for Fe_3O_4 . Ultimately, accumulation of errors resulted in a noticeable discrepancy in the Gibbs energy of formation for BFO from elemental materials ($\sim 10\%$).

Lines 1-3 at the phase diagrams presented in Fig. 1 and 3 represent iron oxides (FeO , Fe_2O_3 , and Fe_3O_4). Precipitation of the oxides occurs at these lines. According inequalities (10) stability regions for the ferrates (LFO and BFO) lay below these lines. (The presented phase diagrams are described in details in the next subsection).

At high oxygen chemical potential iron oxidizes to Fe(III) and exists in the form of Fe_2O_3 . When $\Delta\mu_{\text{O}}$ larger than crossing point of precipitation lines for Fe_2O_3 and Fe_3O_4 , Fe_2O_3 is more stable than Fe_3O_4 . Below this crossing point iron exists in the form of Fe_3O_4 . At this point both Fe_2O_3 and Fe_3O_4 oxides coexist. The values of oxygen atoms chemical potentials at this and other significant crossings of precipitation lines are collected in Table XI.

At the diagrams built on the ground of experimental data the line representing FeO is always above the lines representing Fe_2O_3 and Fe_3O_4 , what means that FeO cannot be stable (but can be metastable) at any temperature and oxygen partial pressure; full reduction of Fe to metallic phase occurs at higher $\Delta\mu_{\text{O}}$ than FeO can become stable. If the diagrams are built using the formation energies obtained from calculations, the line corresponding to FeO crosses the line corresponding to Fe_3O_4 . The later suggests that FeO becomes stable at O chemical potential lower, than these line cross.

Complete reduction of iron is reached at the point where precipitation line for respective oxide crosses the axis at $\Delta\mu_{\text{Fe}} = 0 \text{ eV}$ (which is precipitation line for pure Fe).

2. LaFeO_3

The calculated energy of formation and the Gibbs energy for creation LFO out of elemental materials seems to well reproduce respective experimental data shown in Table IX. However, the same energies for creation a perovskite out of oxides (La_2O_3 and Fe_2O_3) are much more sensitive to accuracy of applied computational or experimental techniques because it involves subtraction of energies of formation of the oxides from the energy for the perovskite, where all three values appeared to be relatively large in comparison to the final result. Such situation can result in poor accuracy of the obtained energies of formation

from oxides. As it was mentioned in Introduction, there is a large spread of experimental values⁹⁻¹⁴ for Gibbs free energy of formation of LFO from the oxides due to various possible deficiencies in employed measurements methods. Here we selected a few experimental results obtained by the most careful approaches. We selected one value (-0.66 eV) obtained from electrochemical technique¹⁰, which explicitly tried to avoid shortcomings of other electrochemical measurements. And two other values were obtained combining enthalpy of formation LFO from the oxides measured by high-temperature oxide melt solution calorimetry¹¹ and entropy of formation obtained by adiabatic calorimetry¹² (-0.68 eV) or by calvet calorimetry¹³ (-0.74 eV). All these experimental Gibbs energies of formation appeared to be reasonably consistent among themselves. The calculated here values (-0.56 – -0.63 eV) are smaller in magnitude by not more than 30% ; Gibbs energies of formation calculated without f-orbitals at La are ~17% larger than the energies calculated with these orbitals. It also has to be noted that the energies of formation from the oxides are important also because they determine the width of the stability region in the phase diagrams, shown on the figures in this paper.

The calculated and experimental energies of formation were used to build the phase diagrams in Fig. 1. This figure contains the diagrams built on calculations with f-orbitals in basis set at La. The diagrams based on calculations without f-orbitals at La are similar to the presented at Fig. 1. Therefore, they are left in Supplemental Materials.⁵⁵ Each of the phase diagrams here is composed from three panels. The phase diagrams are plotted in the center panels. The numbered lines represent conditions for precipitation of La metal, La and Fe oxides, and LFO according Eqs. (9)-(11). The green areas represent the region of the LFO stability defined by conditions in Eqs. (7)-(11). Our theory assumes that within the stability regions a stoichiometric ratio of metals is strictly preserved or, in other words, the number of La and Fe atoms is equal and no defects are created. This restriction is, obviously, an idealization and one of our basic approximations. Under this condition, the external environment (temperature T and partial oxygen pressure p_{O_2}) determine only the sum of metal's chemical potentials, according to Eqs. (3) and (5). The chemical potentials of the involved metal atoms could be determined separately, provided at least one additional material exists in the system.

If a system contains more Fe atoms than La atoms, the excess Fe atoms will be oxidized and present as one of iron oxides depending on oxidizing conditions (temperature and oxygen gas partial pressure). The chemical potentials of Fe and O atoms ($\Delta\mu_{Fe}, \Delta\mu_O$) will lay at the right boundary of the stability region; then corresponding chemical potential of La atoms $\Delta\mu_{La}$ can be determined from Eq. (5). At high oxygen chemical potential iron oxidizes to Fe(III) and exists in the form of Fe_2O_3 . On the way down to lower values of oxygen chemical potential iron reduces. The evolution of the iron oxides is described in the previous subsection. After complete reducing of the excess iron there is still a range of chemical potentials where LFO yet stable and LFO coexists with pure Fe. While the upper boundary of this range is defined by the point where excess Fe atoms fully reduced, the lower boundary corresponds to the crossing of precipitation line for La_2O_3 with the $\Delta\mu_O$ axis ($\Delta\mu_{Fe} = 0 eV$), which corresponds to precipitation of pure iron metal. At this point LFO decomposes to lanthanum oxide La_2O_3 , pure iron and oxygen gas ($4LaFeO_3 \rightarrow 2La_2O_3 + 4Fe + 3O_2$).

If there is excess of La atoms in the system, these atoms are oxidized too and exist in form of La_2O_3 oxide. LFO and La_2O_3 will co-exist in equilibrium. Chemical potentials ($\Delta\mu_{Fe}, \Delta\mu_O$) lay at the left boundary of LFO stability region. Such situation will continue during decrease of O atoms' chemical potential until the precipitation line for La_2O_3 will cross the precipitation line for pure Fe, where the same reaction of LFO decomposition will occur.

In the case where the number of La and Fe atoms in the system will be equal, what is stoichiometric ratio in LFO, only LFO should exist and chemical potentials ($\Delta\mu_{Fe}, \Delta\mu_O$) will belong to LFO stability region. Decrease of O atoms' chemical potentials causes movement of ($\Delta\mu_{Fe}, \Delta\mu_O$) point inside the stability region down until it will reach the lowest point of the stability region, where LFO will decompose the same way as in the previous cases.

Overall, the obtained from presented calculations range of the O atom chemical potentials, where the LFO exists and stable, and obtain is only by $\sim 0.1 eV$ narrower than derived from the experimental energies of formation what is pretty good agreement.

Two side panels in the phase diagrams such as in Fig.1 serve for a conversion of oxygen atom chemical potential to the observable values, which are temperature and oxygen gas partial pressure here. Variation of the oxygen chemical potential, Eq. (3), is plotted in both side panels. On the right panels the oxygen chemical potential is presented as a function of

temperature for a set of selected oxygen gas pressures, so that each line corresponds to a given pressure. Instead, on the left panel the oxygen chemical potential is presented as a function of gas pressure for a given set of temperatures, with the temperature increment of 100 K. These panels could be used in two ways. One can draw vertical lines on the panels for a selected temperature (on the right panel) or pressure (on the left panel). This is illustrated by vertical lines at side panels in Fig. 1a. Crossings between these vertical lines and the functions plotted at the panels allow us to determine the pressure (temperature) for the selected temperature (pressure) at the right (left) panel, correspondingly. Alternatively, if temperature (pressure) at a specific pressure (temperature) for a point in the phase diagram has to be determined, a horizontal line could be drawn through this point, then the temperature (pressure) sought for can be found at the crossing of this horizontal line with the line for desirable pressure (temperature) at the right (left) panel. This approach is illustrated in Fig. 1a by a broken horizontal line and vertical arrows. As it can be seen from these side panels increase of temperature and/or decrease of oxygen partial pressure causes decrease of chemical potential for O atoms $\Delta\mu_{\text{O}}$.

The phase diagrams in Fig.1 allow us to analyze the equilibrium between compounds as a function of chemical potentials and to determine the range of the chemical potentials where relevant compounds are stable. However, despite this range of measurable environmental parameters (T, p_{O_2}) is indirectly defined though the chemical potentials, it is not trivial to extract it from such diagrams. It is much more convenient to mark the window of LFO stability at the maps of the chemical potentials, which are functions of the environmental variables, as defined by Eq. (3). Such contour maps for the all-electron calculations and experimental data are plotted in Fig. 2. As before, this figure contains maps drawn using experimental data and the calculated energies obtained employing all-electron basis set at Fe and the basis set for La which contains f-orbitals. The rest of maps can be found in Supplemental Materials⁵⁵ at Fig. S3.

Each contour line in Fig. 2 and S3 corresponds to a constant value of $\Delta\mu_{\text{O}}$, ranging between 0 eV and -8 eV with the increment of -0.5 eV. The lower boundary of the stability region for LFO is defined by the oxygen chemical potential, where the material

decomposes. The upper boundary of the LFO stability is the line for $\Delta\mu_{\text{O}} = 0 \text{ eV}$, as follows from the phase diagrams in Fig. 1.

The stability regions in Figs. 2 and S3 are shown in green. Additional lines are also shown in these maps. The dotted line corresponds to the oxygen chemical potential, where the oxidation state of Fe changes and two oxides Fe_2O_3 and Fe_3O_4 coexist. In the case of iron excess, this line divides the stability region into the two areas: the area where LFO coexists either with Fe_2O_3 , or the area where it coexists with Fe_3O_4 . At this line LFO is in equilibrium with both oxides. The dot-dashed additional line in the maps in Figs. 2 and S3 corresponds to the oxygen chemical potential at which the second iron reduction step from Fe_3O_4 to FeO occurs. This line separates areas, where LFO co-exists with one of these oxides; all three materials (LFO, Fe_3O_4 and FeO) co-exist at this line. The dot-dashed line is not present at the map based on experimental data because FeO never becomes stable, as it was noted above. The dashed line marks O atoms' chemical potential $\Delta\mu_{\text{O}}$, where complete reduction of Fe takes place. Below the later line LFO co-exists with pure non-oxidized iron until chemical potential for O atoms $\Delta\mu_{\text{O}}$ reaches point of LFO decomposition. At this line LFO co-exists with both pure iron and respective iron oxide. The values of chemical potential for O atoms $\Delta\mu_{\text{O}}$ corresponding to all these lines and the lower boundary of LFO stability region can be found in Table XI.

3. *BiFeO₃*

The calculated energies of formation and the Gibbs energies for BFO formation from Bi_2O_3 and Fe_2O_3 are only -0.05 eV , hence considerably underestimated with respect to the enthalpies of formation calculated from the experimental data.^{15,65} However, these Gibbs energies of formation still have correct sign indicating a weakly stable BFO with respect to its decomposition into Bi and Fe binary oxides. A large deviation in the energy of formation for BFO from the binary oxides could arise for two reasons: (i) due to shortcoming of the used B3PW hybrid density functional, or (ii) neglect of the phonon contributions to the energies of formation. However, based on the experimental temperature dependence of the energy of formation for BFO¹⁵ and those for Bi_2O_3 and Fe_2O_3 ⁶⁵, one can conclude that the contribution of the phonons to the BFO energy of formation from the oxides is negligible

(of the order of 0.03 eV in the wide temperature range from room to 1200 K). This is why we believe that limitations of the employed functional bear primary responsibility for the underestimate of this energy of formation therefore, further testing of available hybrid functionals has to be performed soon.

A similar estimate performed with the LDA+U method and plane wave basis set for the BFO energy of formation from the binary oxides yielded -0.2 eV.²³ This value is more negative than that in our calculations but still much smaller compared to the experimental results¹⁵ (-0.7 eV).

The respective subset of calculated and experimental energies of formation from TABLE IX is used to build the phase diagrams (Fig. 3) similar to the diagrams built for LFO (Fig. 1). Design of these diagrams is described in the previous subsection. As before, BFO stability region is colored in green. It is limited on top by precipitation lines for iron oxides, on right by Fe precipitation line, and below by Bi₂O₃ and Bi precipitation lines.

Due to much smaller energies gained at oxidation of Bi and respectively smaller Gibbs energy of formation for BFO in comparison to the one for LFO, Bi precipitation line lays at significantly higher O atoms' chemical potentials. La precipitation line in the diagrams for LFO is located much lower than La oxide precipitation line and LFO stability region, but Bi precipitation line runs right through BFO stability region and crosses Bi₂O₃ precipitation line. Moreover, Bi precipitation line crosses Fe precipitation line above the chemical potential $\Delta\mu_o$ where complete reduction of iron occurs. All these means that Bi completely reduces at larger $\Delta\mu_o$ (smaller temperatures T and/or larger oxygen gas partial pressures p_{O_2}) than Fe.

In the systems with more Fe atoms than Bi atoms, the excess Fe atoms are present in the oxidized form as Fe₂O₃ or Fe₃O₄ oxides. This corresponds to the right boundary of BFO stability region. Which of these two oxides is formed, depends on the oxygen chemical potential. At high oxygen chemical potential iron oxidizes to Fe(III) and exists in the form of Fe₂O₃ and BFO co-exists with this oxide. In the diagrams based on experimental data or on the calculations which use all-electron basis set on Fe the crossing of precipitation lines for Fe₂O₃ and Fe₃O₄ occurs above Bi precipitation line. Such location of the crossing point suggests that reduction of iron oxide from Fe₂O₃ to Fe₃O₄ can happen while BFO can exist

and is still stable. At the crossing point all three BFO and both Fe₂O₃ or Fe₃O₄ oxides co-exist. Below the crossing point BFO co-exists only with Fe₃O₄ oxide. Further reduction of O atoms' chemical potential $\Delta\mu_O$ brings such a system to the crossing with Bi precipitation line. Above this point BFO still co-exists with Fe₃O₄. In the later crossing point BFO decomposes to Fe₃O₄ and metallic Bi with emission of oxygen gas ($3BiFeO_3 \rightarrow Fe_3O_4 + 3Bi + O_2$). Since the precipitation lines for Fe₃O₄ and FeO cross below the precipitation line for Bi metal, coexistence of FeO and BFO does not occur under thermodynamic equilibrium conditions. Of course, FeO can be found at $\Delta\mu_O$ larger than mentioned limits, but under such conditions this oxide has to be metastable and can exist for a long time usually due to slow diffusion kinetics.

In the diagram obtained from calculations with the ECP, the precipitation lines for Fe₂O₃ and Fe₃O₄ cross below the line for precipitation of metallic Bi which means that in the entire range of BFO stability it could be in equilibrium only with more stable Fe₂O₃ oxide until the crossing with Bi precipitation line where decomposition to Bi metal, the O₂ gas and the same Fe₂O₃ oxide ($4BiFeO_3 \rightarrow 2Fe_2O_3 + 4Bi + 3O_2$). In the latter case neither Fe₃O₄ nor FeO could be in equilibrium with BFO.

When there are more Bi atoms than Fe atoms in the system, excess Bi atoms form oxide (Bi₂O₃ here). In this case both Bi₂O₃ and BFO coexist, what corresponds to the left boundary of the stability region (line 4 in Fig.1). Bi₂O₃ exists while $\Delta\mu_O$ decreases, until the crossing with the Bi precipitation line (line 5) at $\Delta\mu_O = \frac{1}{3}\Delta E_{f,Bi_2O_3}$, in all three models considered here, because the same Gibbs energy of formation is used in all models. Following this decrease of the O atoms' chemical potential $\Delta\mu_O$, the system moves in the phase diagram along the left boundary of the stability region. At the crossing point of Bi₂O₃ and Bi metal precipitation lines Bi₂O₃ reduces to a metallic Bi. When this process is completed, further decrease of $\Delta\mu_O$ becomes possible. Following this change in $\Delta\mu_O$, the system will move along the bottom section of the stability region boundary defined by the Bi precipitation line. Correspondingly, while this segment will be passed, BFO coexists with Bi metal. Finally, upon reaching the crossing with Fe₃O₄ precipitation line BFO will decompose on Fe₃O₄, Bi metal and oxygen gas ($BiFeO_3 \rightarrow Fe_3O_4 + 3Bi + O_2$) if the all-electron calculations or experimental energies of formation are used. The results for the ECP calculations differ

from the all-electron calculations only by the iron oxide products of the decomposition of BFO, which in this case is Fe_2O_3 ($4\text{BiFeO}_3 \rightarrow 2\text{Fe}_2\text{O}_3 + 4\text{Bi} + 3\text{O}_2$).

When the number of Bi and Fe atoms is equal in the stoichiometric BFO and $\Delta\mu_{\text{O}}$ decreases, the system moves through the stability region to its lowest point, where the precipitation lines of Bi metal and Fe_3O_4 (in the all-electron calculations and for experimental data) or Fe_2O_3 (the ECP calculations) are crossing. And, as in the previous cases, BFO decomposes into Bi metal, the O_2 gas and Fe_3O_4 or Fe_2O_3 .

In all possible cases, irrespective of either excess of Fe or Bi atoms or their stoichiometric ratio, Bi is reduced to a metal, while Fe either not reduced at all (Fe_2O_3 in the ECP based model) or gets reduced only to Fe_3O_4 (two other models). In our calculations the range of the O atom chemical potentials, where the BFO exists and stable, is by $\sim 0.4\text{-}0.5$ eV narrower than derived from the experimental energies of formation.

As before, to show the region of stability BFO in experimentally accessible environmental values (T, p_{O_2}) we drew contour maps like ones drawn for LFO. The ranges of BFO stability in both the ECP and all-electron calculations are very close: it decomposes at $\Delta\mu_{\text{O}} = -2.02$ eV, or at $\Delta\mu_{\text{O}} = -2.0$ eV, respectively. Therefore, both contour maps are very similar and only the latter is shown in Fig. 4, the results for the calculations with ECP are given in Fig. S4 in Supplementary Materials.⁵⁵

The stability regions in Figs. 4 and S4 are shown in green. Two additional lines are also shown in the maps of Fig. 4. The dotted line corresponds to the oxygen chemical potential, where the oxidation state of Fe changes and two oxides Fe_2O_3 and Fe_3O_4 coexist. In the case of iron excess, this line divides the stability region into the two areas: the area where BFO coexists either with Fe_2O_3 , or the area where it coexists with Fe_3O_4 . At this line BFO is in equilibrium with both oxides. (This line does not appear in the map for the ECP calculations, because here Fe reduction occurs outside the stability region.) The second, dashed additional line in the maps in Fig. 2 corresponds to the oxygen chemical potential at which Bi oxidation/reduction occurs. As mentioned earlier, above this line BFO is in equilibrium with Bi_2O_3 , below this line it coexists with metallic Bi, and at this line all three materials BFO, Bi_2O_3 and metallic Bi are in equilibrium. Since the oxygen chemical potential

at this line is $\Delta\mu_o = 1.99 \text{ eV}$ and thus very close to the counter line for $\Delta\mu_o = 2.00 \text{ eV}$, the latter contour line is replaced by the dashed line. Also, the difference between the oxygen chemical potential for Bi reduction/oxidation and for the BFO decomposition differ only by 0.03 eV (for all-electron calculations), the dashed line practically coincides with the boundary of the BFO stability region. In reality the gap between these lines is too narrow to allow their distinction.

As a final note, the present modeling explicitly shows the sequence(order?) of the chemical potentials for O atoms $\Delta\mu_o \Delta\mu_o^M$ which correspond to complete reductions to metallic state for all involved metals. Also, it is straightforward to point location in this sequence for the chemical potentials for O atoms $\Delta\mu_o^{LFO}$ and $\Delta\mu_o^{BFO}$, at which decomposition of the considered perovskites takes place:

$$\Delta\mu_o^{Bi} > \Delta\mu_o^{BiFeO} > \Delta\mu_o^{Fe} > \Delta\mu_o^{LaFeO} > \Delta\mu_o^{La} . \quad (14)$$

4. CONCLUSIONS

The atomic structures of LaFeO_3 and BiFeO_3 and the possible products of its decomposition (La_2O_3 , Bi_2O_3 , FeO , Fe_2O_3 , Fe_3O_4) were optimized, and the total energies for these structures were calculated by means of the B3PW hybrid density functional. To maximize the accuracy of these calculations, the localized basis sets for all involved atoms were re-optimized. To save computer resources, scalar-relativistic energy-consistent ECPs were used for metal atoms whereas the all electron basis set used for O atoms. For Fe atom both ECP and all-electron calculations were performed and carefully compared. The calculated atomic structures for different phases of La_2O_3 , Bi_2O_3 , FeO , Fe_2O_3 , Fe_3O_4 and their sequence in energies are in good agreement with experiments. Use of ECP or neglect with f-orbitals in basis set of La lead to a small increase in lattice constants of all modeled materials. Removal of f-orbitals from basis set at La causes also reduction of the energies of formation for LFO by $\sim 0.05\text{eV}$.

The performed calculations yielded the Gibbs energies of formation for these compounds, from which the phase diagram and stability boundaries of LFO and BFO were determined. An analogous diagram was constructed using the experimental Gibbs energies of formation. These diagrams allow us the understanding of possible chemical

transformations in the system, whenever the system contains equal numbers of La or Bi and Fe atoms or there is an excess of one of these metals.

According to all phase diagrams for LFO excess of Fe or La atoms in the system are present in the form of respective oxides, while specific form of Fe oxide depend on O atoms chemical potential. The phase diagrams built on calculated energies of formation suggest an existence a range of chemical potential of O atoms where FeO is stable and can co-exist with LFO. This contradict to the diagram based on experimental data, where FeO precipitation line is located always above precipitation lines for the most stable iron oxide at each possible environmental conditions and, correspondingly, above the region of LFO stability. Anyway, the final decomposition of LFO at sufficiently low chemical potential of O atoms $\Delta\mu_O$ produces La_2O_3 , pure iron and O_2 gas. Complete reduction of iron occurs at higher values of O atoms' chemical potential then LFO decompose.

The experimental phase diagram indicates that stoichiometric BFO decomposes to Fe_3O_4 , metallic Bi, and O_2 gas when the oxygen chemical potential is decreased (either by increasing the temperature and/or decreasing the oxygen partial pressure). The same result is obtained for Fe atom treatment with all-electron basis set (and thus, without assistance of the pseudopotentials, ECP.) In both cases, upon excess of Fe atoms, Fe_2O_3 reduces to Fe_3O_4 before the oxygen chemical potential reaches the critical value of BFO decomposition. In turn, in the phase diagram for the ECP on Fe the point, where such an iron reduction occurs, lies outside the BFO stability region. This result indicates that the decomposition of BFO in the presence of excess Fe should produce Fe_2O_3 instead of Fe_3O_4 . If the system contains an excess of Bi atoms, the reduction of excess Bi from Bi_2O_3 to a pure metallic Bi state occurs, also prior to the point when BFO starts to decompose.

The ranges of oxygen chemical potentials in which LFO and BFO are stable were determined from the phase diagrams and drawn as a contour maps. This allowed us to employ the state-of-the-art methodology for the analysis of advanced materials stability and to compare theoretical prediction of the regions, where LFO and BFO are stable in terms of temperature and oxygen partial pressure, with the experimental data.

Our refined hybrid B3PW calculations with carefully optimized basis sets still significantly underestimate the BFO energy of formation in comparison with the experimental value, similarly to the much simpler LDA+U results. This underestimate leads

to a very narrow range of BFO stability that is determined here by the energy of formation of BFO from Bi_2O_3 and Fe_2O_3 . This could be explained by the shortcomings of the employed B3PW hybrid functional further testing of available hybrid functionals would be needed. It should be noted also that the available experimental data on BFO decomposition into binary oxides are very limited additional studies on both BFO and other perovskites decomposition are necessary, along with theoretical calculations at different levels, in order to draw more reliable conclusions. Hopefully this testing will also allow improving results for LFO, where some underestimate of the energies of formation is present, while on much smaller scale.

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