Stability Analysis of SrFeO3, BaFeO3, BiFeO3, and LaFeO3 perovskites using *ab initio* calculations with B3PW hybrid functional.

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Approach

- Yu. A. Mastrikov, et al. , *J. Phys. Chem. C*, **114**, *3017–3027* (2010).

- E. Heifets, E. A. Kotomin, Yu. A. Mastrikov, S. Piskunov, J. Maier, “Thermodynamics of ABO_3-type Perovskite Surfaces” in: *Thermodynamics - Interaction Studies - Solids, Liquids and Gases*, edited by J.C. Moreno, InTech, November, 2011; http://www.intechopen.com/articles/show/title/thermodynamics-of-abo3-type-perovskite-surfaces

- M. Kuklja et al, PCCP (Perspective) 15, 5443 (2013)

Motivation

- We consider a set of materials ($SrFeO_3$, $BaFeO_3$, $LaFeO_3$,$BiFeO_3$) , which are limiting for solid solutions employed as the most presently efficient cathode materials in solid oxide fuel cells (SOFCs) : $Ba_{0.5}Sr_{0.5}Fe_xCo_{1-x}O_3$, $La_{0.8}Sr_{0.2}Fe_xCo_{1-x}O_3$, and a new recently proposed $Bi_{1-y}Sr_yFe_xCo_{1-x}O_3$

  (A. Wedig, PhD thesis, MPI for Solid State Research, Stuttgart, Germany, 2013, http://elib.uni-stuttgart.de/opus/frontdoor.php?source_opus=8622&la=de).

- What conditions (partial pressure and temperature of oxygen gas) are required to insure existence and stability of a target material with respect to decomposition to simple oxides and metals?
- What are conditions allowing to produce a material?
- How to estimate such conditions from results of ab initio calculations?
- Determine region of chemical potentials of components where considered material exists and there is a sense to analyze surface structures, their stability, formation of defects, and reactions at crystal surfaces.

Computational details

- CRYSTAL09 code: Local Gaussian type basis set
- Stuttgart ECP at Bi, La, Sr, Ba; all-electron and Stuttgart ECP at Fe; all-electron at O.
- Basis sets optimized in forms:
  - s411p411d411 (with ECP at Fe, La) ,
  - s411p411d411f11 (with ECP at La),
  - s411p411d11 (with ECP at Sr, Ba),
  - s4411p411d411 (with ECP at Bi) ,
  - s86411p6411d411 (all-electron at Fe),
  - s8sp411d11 (all-electron at O).
- Hybrid density functional: B3PW
- 8x8x8 Monkhorst-Pack net

Some restrictions

Important approximation: $G_{solid} \approx E_{solid}$

Usually good , but fails when soft modes are present.

In $AFeO_3$ (A=Sr, Ba, Bi, La) the chemical potentials are connected by:

$$\mu_A + \mu_{Fe} + \frac{3}{2}\mu_{O2} = G_{AFeO_3} \approx E_{AFeO_3}$$

leaving only two of the chemical potentials as independent variables. We choose : μ_{Fe} and μ_{O2} , which are common for all considered materials.

Deviations of chemical potentials

Deviations of chemical potentials from reference states:

$$\Delta\mu_A = \mu_A - E_A^{bulk}$$

Variations of chemical potentials for atoms A calculated with respect to chemical potential of atom A in metallic phase A metal stable at standard conditions

$$\Delta\mu_O(T,p) = \mu_O(T,p) - \frac{1}{2}E_{O2}$$

Variations of chemical potentials for oxygen atoms are calculated with respect to oxygen atom in O_2 molecule:

Dependence on temperature and pressure

T & p dependencies of μ are usually weak in solids, but strong in gases!

$\mu_A(T,p)$ – neglected;
$\mu_O(T,p)$ defines (T,p) dependence of surface Gibbs free energies.

Ideal gas approximation: $\Delta\mu_O(T,p) = \frac{1}{2}\{\Delta G^{gas}_{O2}(T,p^0) + kT\ln(\frac{p}{p^0})\} + \delta\mu^0_O$

where: $\Delta G^{gas}_{O2}(T,p^0) = G^{gas}_{O2}(T,p^0) - G^{gas}_{O2}(T^0,p^0)$

taken from Thermodynamical Tables.

The correction $\delta\mu_O^0$ matches the origin of the experimental variation of the O chemical potential and the reference point in our theoretical estimates ($E_{O2}/2$).

Energies of metals

Energies of metals
calculated with hybrid functionals
usually are unreliable and bad.

Energies for reference phases of metals can be calculated from each of considered oxides:

$$E_M[M_xO_y] = \frac{1}{x}\left(E_{MxOy} - \Delta H^{0}_{f,MxOy} - \frac{1}{2}\left(E_{O2} + \Delta H^{gas}_{O2}(T^0, p^0)\right)\right)$$

and then averaged:

$$E_M = \frac{1}{n_M} \sum_{M_xO_y} E_M[M_xO_y]$$

Formation energies

Formation energies:

$$\Delta E_{f,MxOy} = E_{MxOy} - xE_{M} - \frac{y}{2}E_{O2}$$

$$\Delta E_{f,AFeO3} = E_{AFeO3} - E_{A} - E_{Fe} - \frac{3}{2}E_{O2}$$

Formation enthalpies:

$$\Delta H^{0}_{f,MxOy} = E_{MxOy} - xE_{M} - \frac{y}{2}(E_{O2} + \Delta H^{gas}_{O2}(T^{0}, p^{0}))$$

$$\Delta H^{0}_{f,AFeO3} = E_{AFeO3} - E_{A} - E_{Fe} - \frac{3}{2}(E_{O2} + \Delta H^{gas}_{O2}(T^{0}, p^{0}))$$

Decomposition conditions

A material is stable = No precipitation of different phases:

Fe metal: $\Delta\mu_{Fe} \leq 0$

A metal: $\Delta\mu_{Fe} + 3\Delta\mu_{O} \geq \Delta E_{f,AFeO_3}$

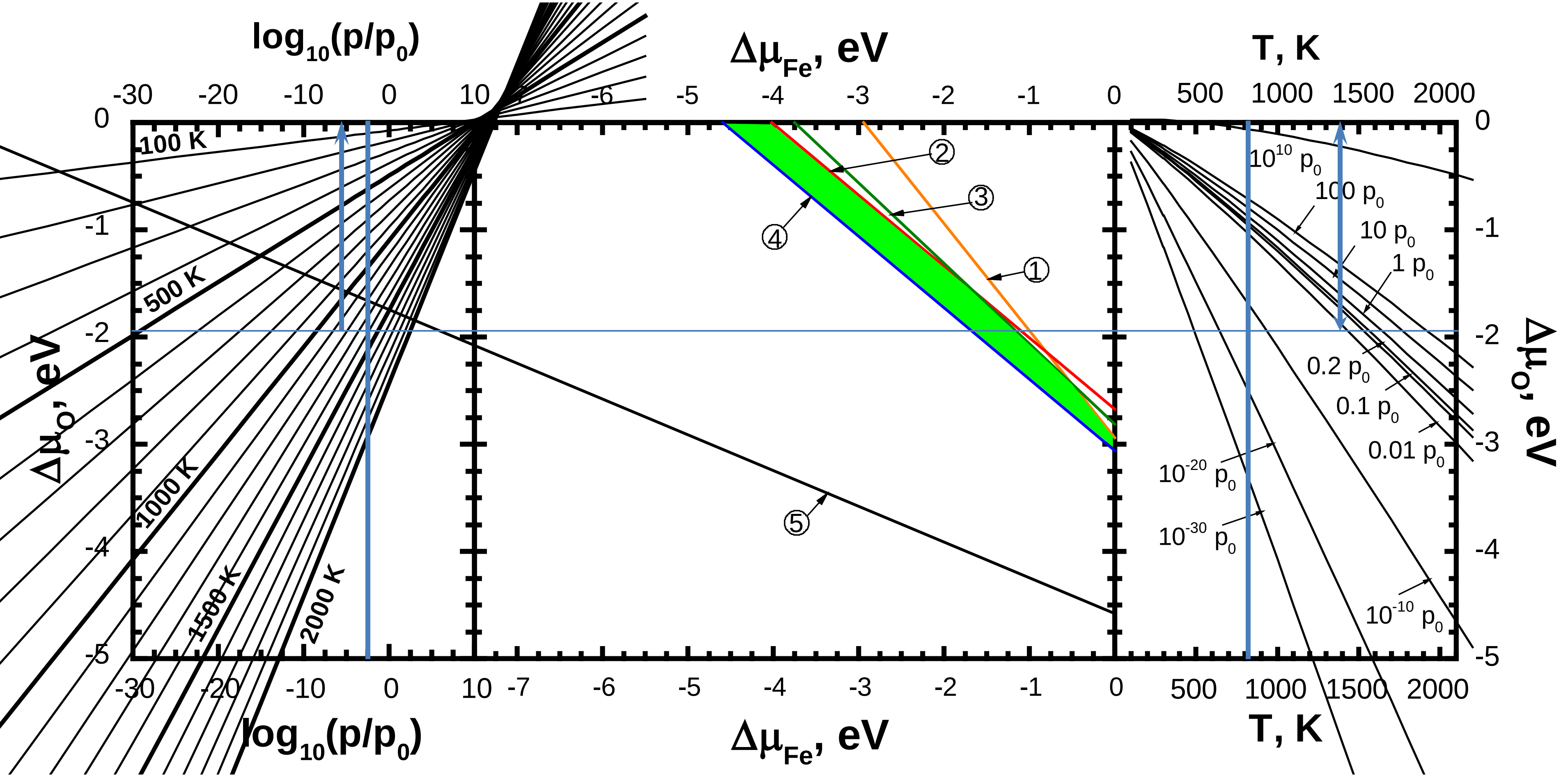
Fe oxides: $x\Delta\mu_{Fe} + y\Delta\mu_{O} \leq \Delta E_{f,Fe_xO_y}$

A oxide: $x\Delta\mu_{Fe} + (3x-y)\Delta\mu_{O} \geq x\Delta E_{f,AFeO_3} - \Delta E_{f,A_xO_y}$

Formation energies

Material	Exprl H^0_f	No Fe		ECP at Fe				All-e at Fe			
		Calc., Direct formulation		Calc., Direct formulation		Calc., Averaged Fe-metal		Calc., Direct formulation		Calc., Averaged Fe-metal	
		ΔE_f	ΔH^0_f	ΔE_f	ΔH^0_f	ΔE_f	ΔH^0_f	ΔE_f	ΔH^0_f	ΔE_f	ΔH^0_f
FeO	-2.82			−4.58	-4.69	-2.89	-2.99	-6.32	-6.42	-2.94	-3.04
Fe_2O_3	-8.56			-11.55	-11.86	-8.17	-8.47	-14.79	-15.09	-8.03	-8.34
Fe_3O_4	-11.62			-16.42	-16.83	-11.17	-11.57	-21.39	-21.80	-11.13	-11.53
Fe_3O_4 (cubic)	-11.62			-15.90	-16.31	-10.82	-11.23	-21.00	-21.41	-11.26	-11.67
FeO_2	-			-	-	-	-	-	-	-	-
Bi_2O_3	-5.95	-5.71	-6.01								
$BiFeO_3$	-????			−8.68	-8.99	-6.96	-7.26	-10.30	-10.60	-6.89	-7.20
La_2O_3	-18.59	-18.28	-18.59								
$LaFeO_3$	-????			-	-	-13.84	-14.14	-	-	-13.78	-14.09
La_2O_3 (f)	-18.59	-18.28	-18.59								
$LaFeO_3$ (f)	-????			-	-	-13.79	-14.09	-	-	-13.73	-14.04
SrO	-6.14	-6.03	-6.13								
SrO_2	-6.57	-6.15	-6.35								
$SrFeO_3$	-????			-11.95	-12.26	-10.36	-10.67	-13.70	-14.01	-10.43	-10.74
BaO	-5.68	-5.71	-5.82								
BaO_2	-6.57	-6.24	-6.44								
$BaFeO_3$	-????			-11.49	-11.79	-9.96	-10.27	-13.22	-13.52	-10.00	-10.31

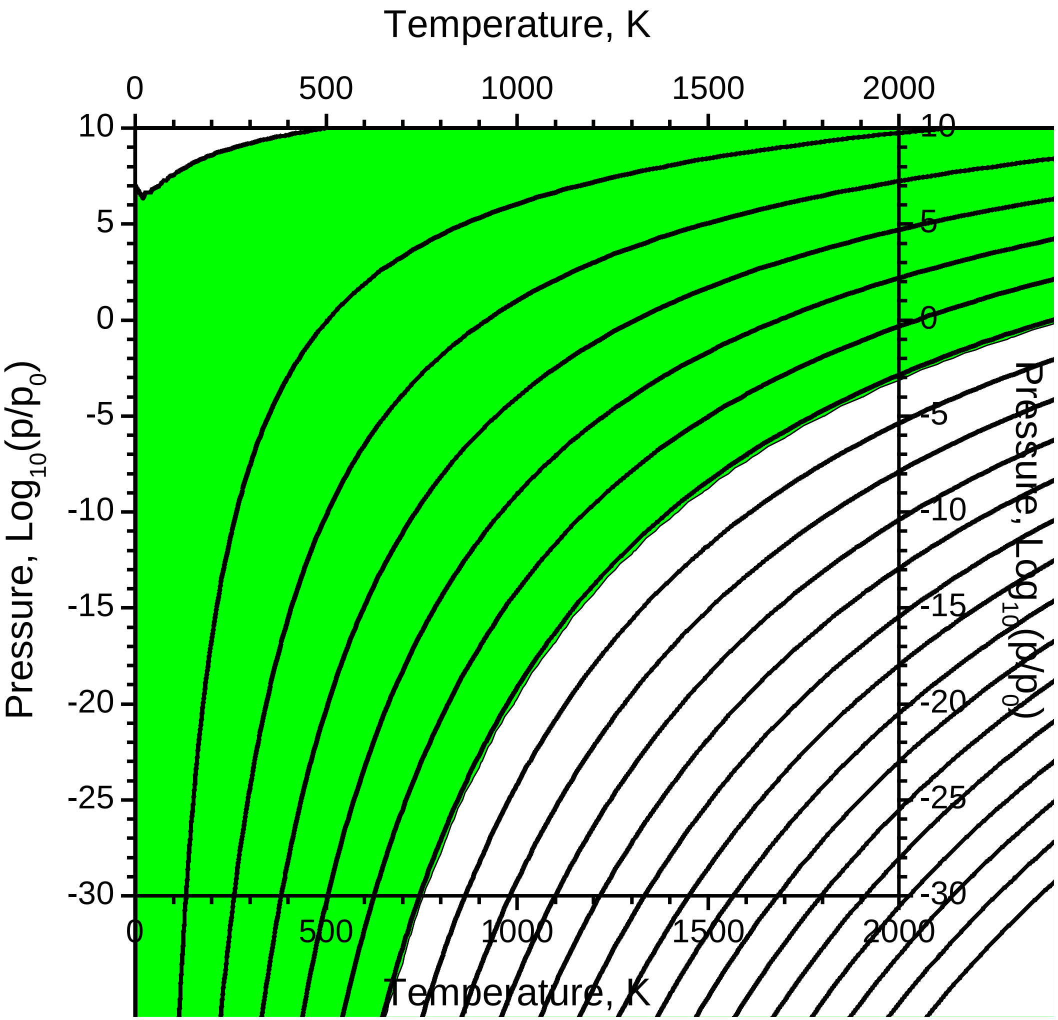
Phase diagram for $LaFeO_3$



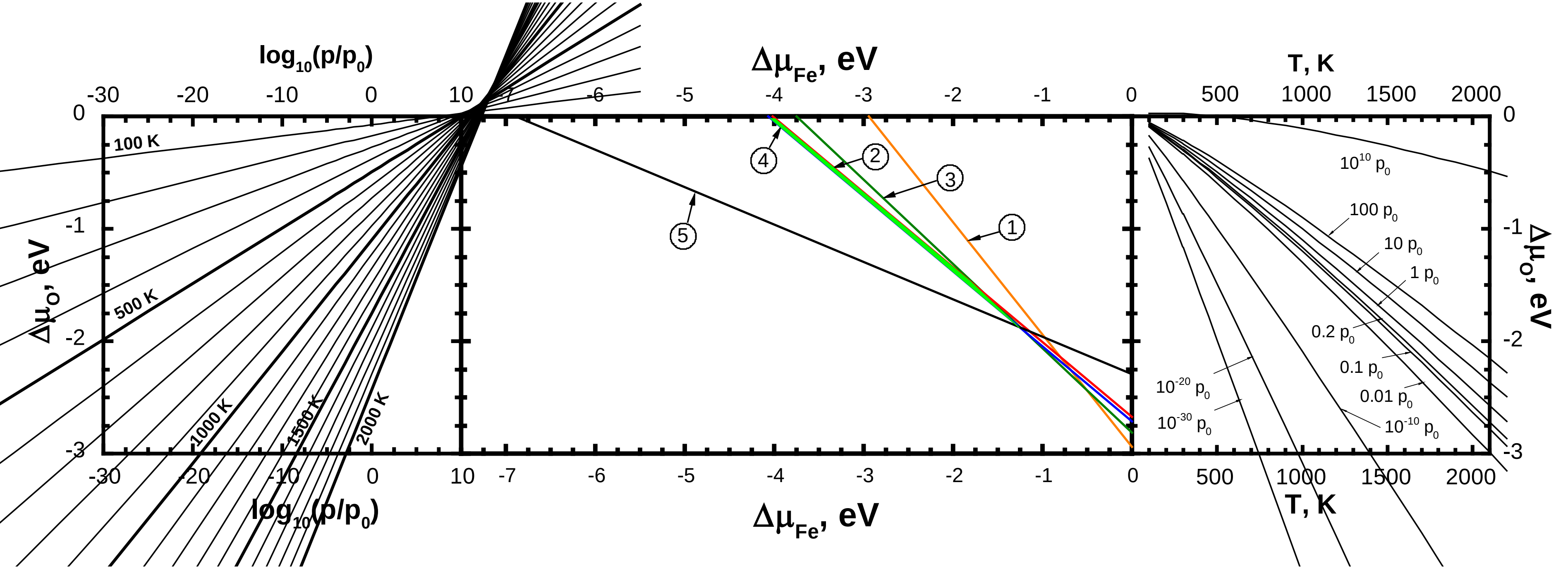
Precipitation of: 1. FeO ; 2. Fe_2O_3 ; 3. Fe_3O_4 ; 4. La_2O_3 ; 5. La metal.
Green region marks the region of stability for $LaFeO_3$

Environmental conditions (T&p_{O2}) allowing existence of $LaFeO_3$

all-electron, B3PW



Phase diagram for $BiFeO_3$

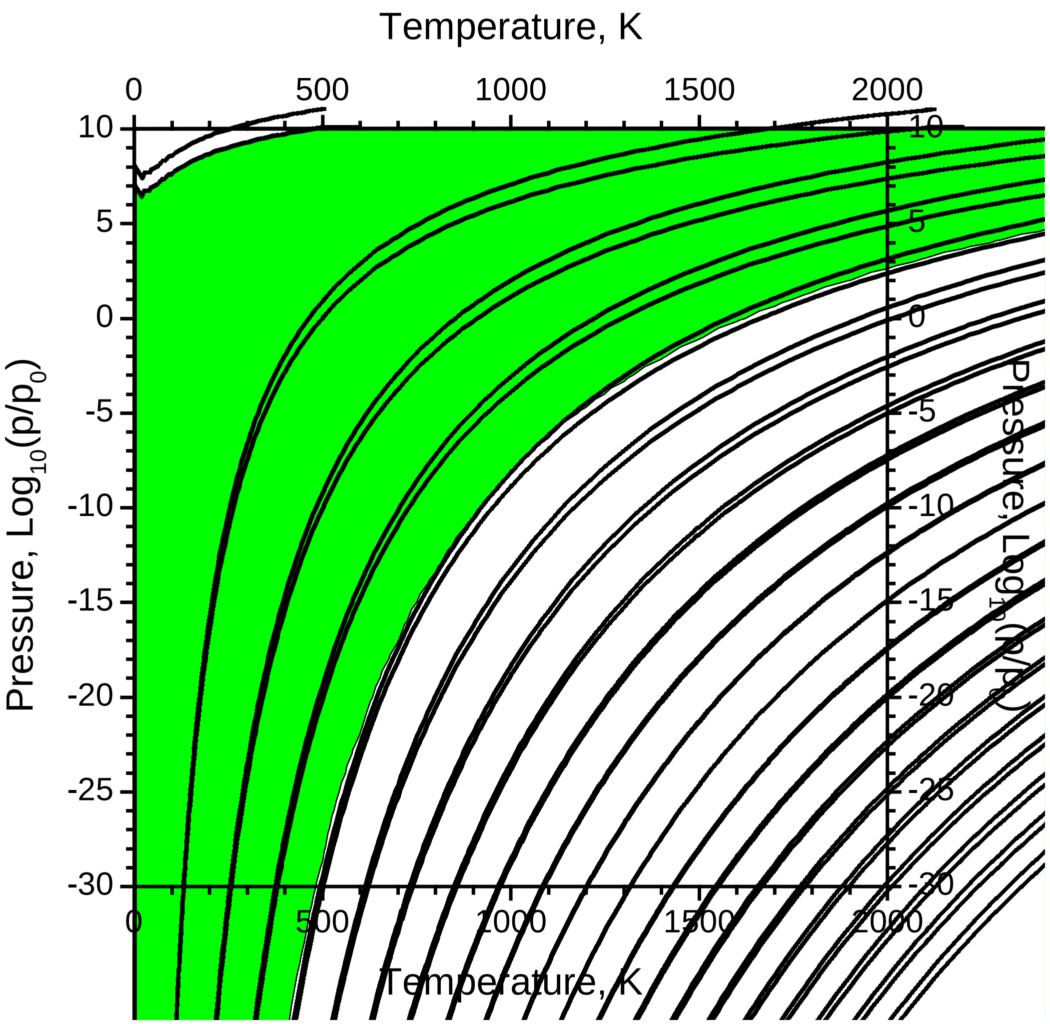


Precipitation of: 1. FeO ; 2. Fe_2O_3 ; 3. Fe_3O_4 ; 4. Bi_2O_3 ; 5. Bi metal.

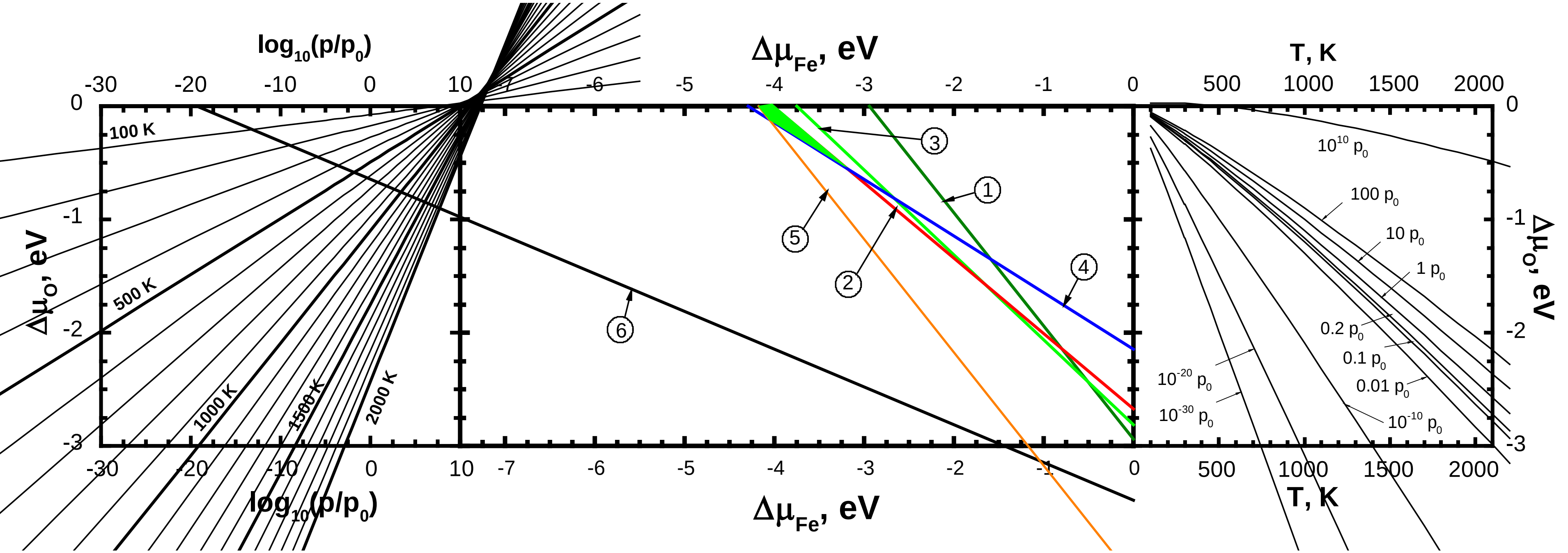
Green region marks the region of stability for $BiFeO_3$

Environmental conditions (T&p_{O2}) allowing existence of $BiFeO_3$

all-electron, B3PW



Phase diagram for $SrFeO_3$



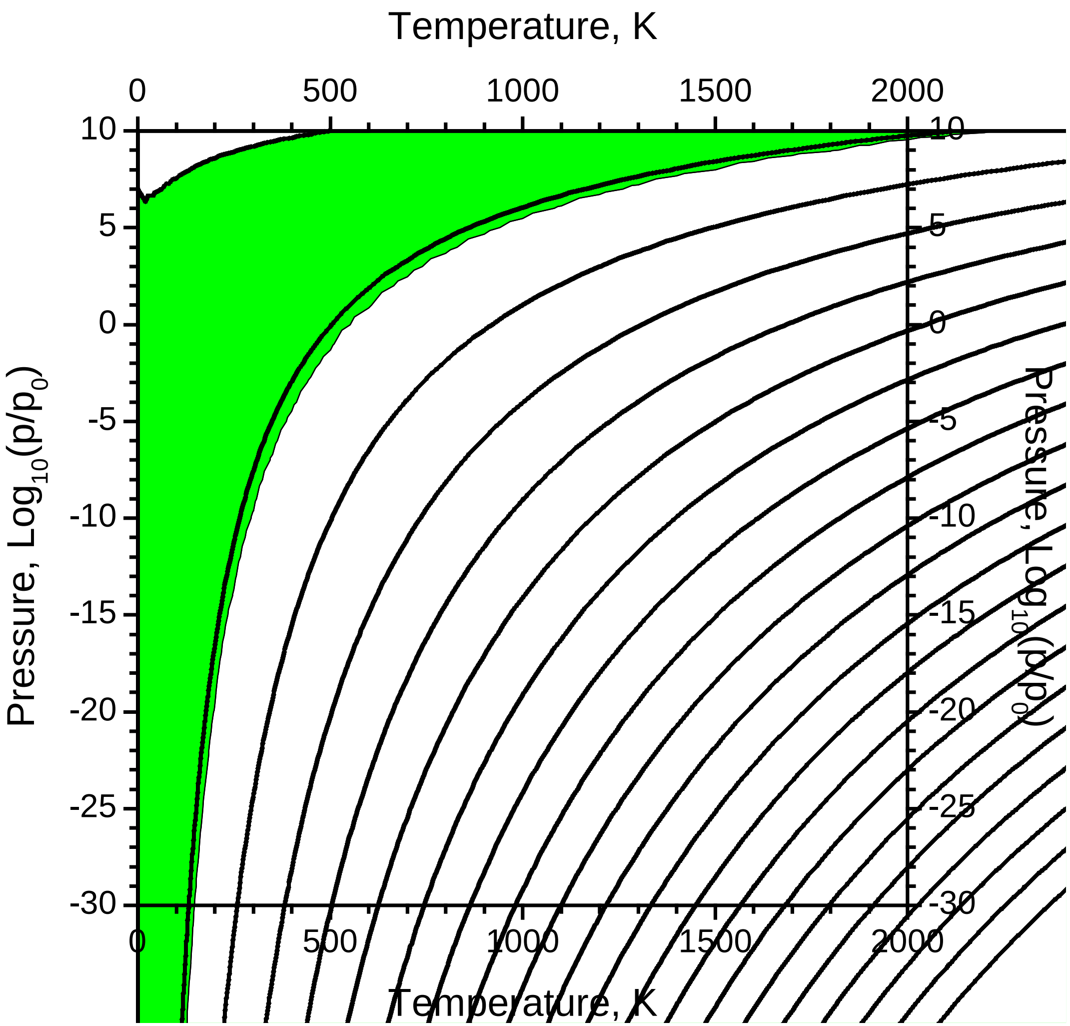
Precipitation of: 1. FeO ; 2. Fe_2O_3 ; 3. Fe_3O_4 ; 4. SrO ; 5. SrO_2 ;

6. Sr metal.

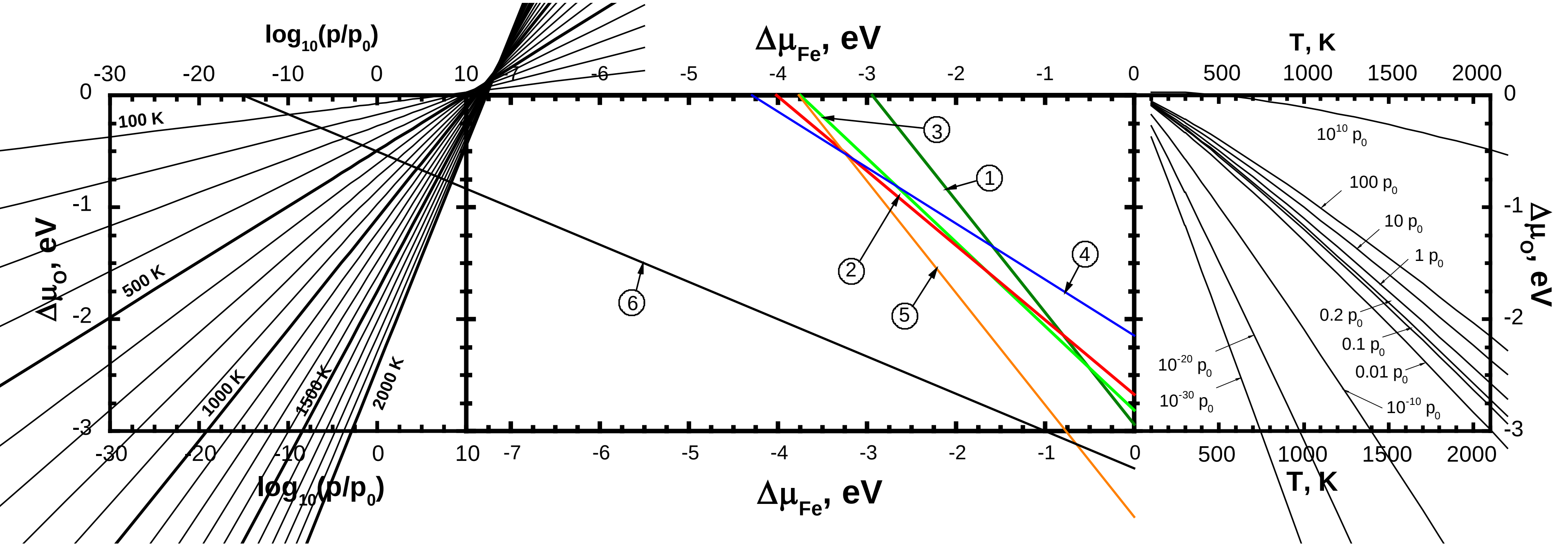
Green region marks the region of stability for $SrFeO_3$

Environmental conditions (T&p_{O2}) allowing existence of $SrFeO_3$

all-electron, B3PW



Phase diagram for $BaFeO_3$



Precipitation of: 1. FeO ; 2. Fe_2O_3 ; 3. Fe_3O_4 ; 4. BaO ; 5. BaO_2 ;

6. Ba metal.

There is not a region of stability of stoichiometric $BaFeO_3$!

Vacancies seem to be necessary to stabilize this material.

Conclusions:

- We were to analyze basic stability and production conditions for synthesis of several perovskite materials using ab initio calculations.
- Created grounds for future analysis of stability of surfaces, modeling oxygen adsorption, formation of O vacancies, mechanism of oxygen reduction reaction and oxygen incorporation into cathode surface.

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Thank you for your

attention!