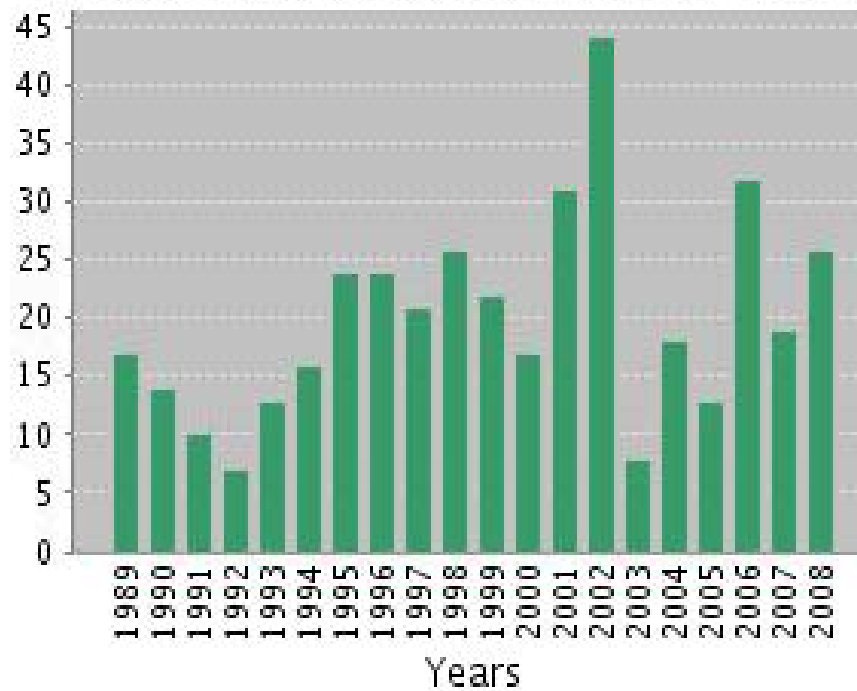


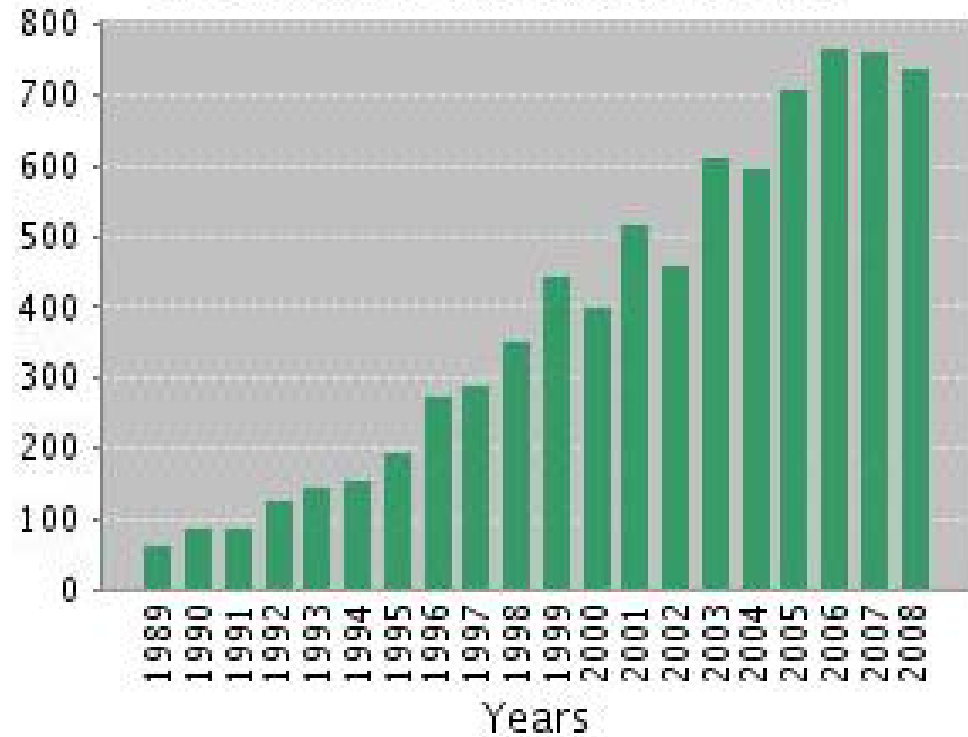
Valence Stability and Madelung Self-Site Potential of Alliovalent Ions in Various Oxide Lattices

Masahiro YOSHIMURA
(Tokyo Institute of Technology, Japan)

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**“Stabilization of High - Valence States of Ions at B - site
of Perovskite Structure ABO_3 : Electrostatic
Potential in Perovskite Structure”**

By

Masahiro YOSHIMURA*, Tetsurō NAKAMURA** and Toshiyuki SATA***

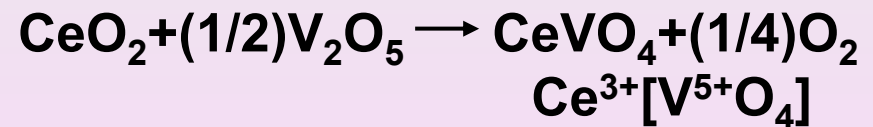
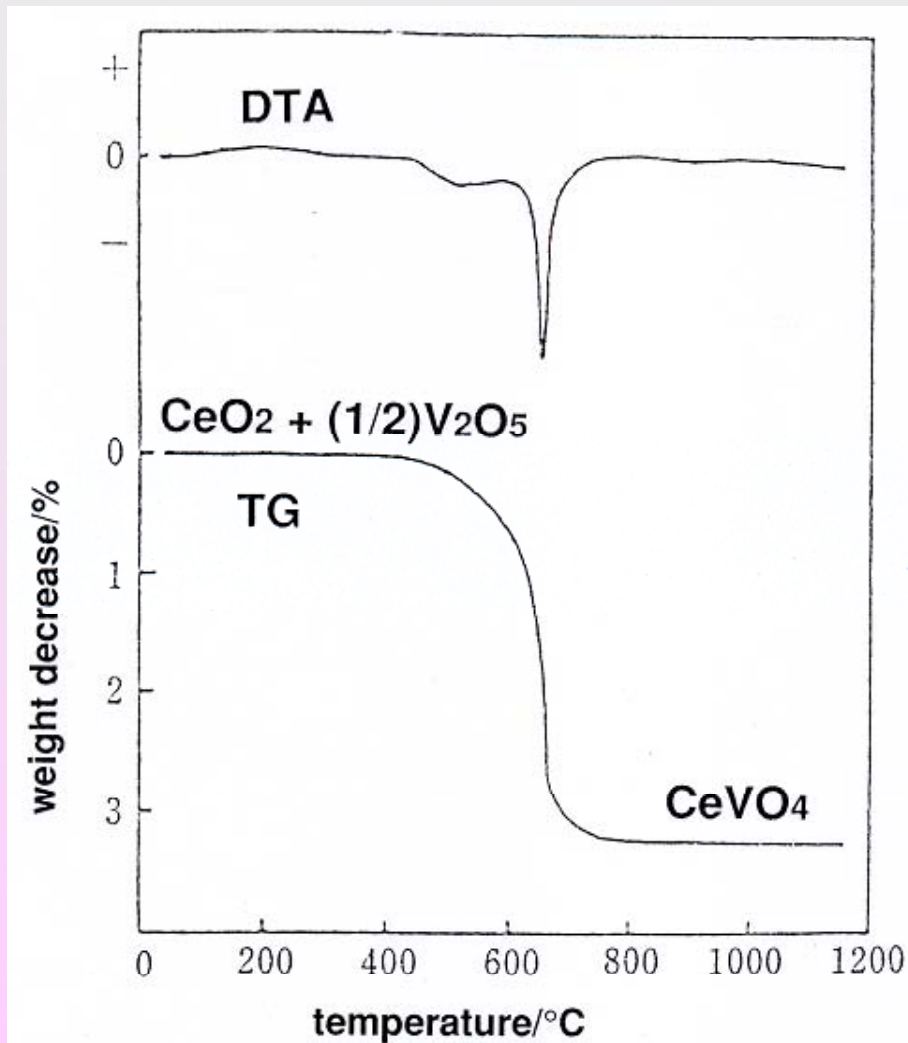
Synopsis

The perovskite-type compounds, $A^{2+}B^{4+}O_3$ ($A = Ba, Sr, B = Ce, Pr, Tb$), were synthesized by the reaction between ACO_2 or AO_2 and B-Oxides. $A^{2+}B^{4+}O_3$ were stable under the conditions where $B^{4+}O_2$ with fluorite structures were no longer stable. This fact was explained by the contribution of lattice energy. That is, the lattice self-potential of B-site in perovskite structure is stronger than that in fluorite structure. It was demonstrated that the stability of valence states of ions was related to the lattice self potentials at those ion-sites in crystal lattices.

From the comparison of the potentials calculated for every sites in several crystal structures, perovskite, corundum, rutile, fluorite etc., it was shown that a certain ion had the maximum potential at B-site of perovskite structures. It was concluded that high valence states were stabilized at B-sites of perovskites which had the strong potentials, even in the cases of other ions, Ni^{3+} , Co^{3+} , Fe^{4+} , Mn^{4+} , etc.

They were also explained by the self-potentials that perovskites would have the point defects at A-sites or oxygen sites, and that $A^{4+}B^{3+}O_3$ type perovskites would not exist.

This was referred
By R.Roy in his
Orton lecture at
Am.Ceram.Soc.
1976,Bull.Am.
Ceram.Soc.(1976)



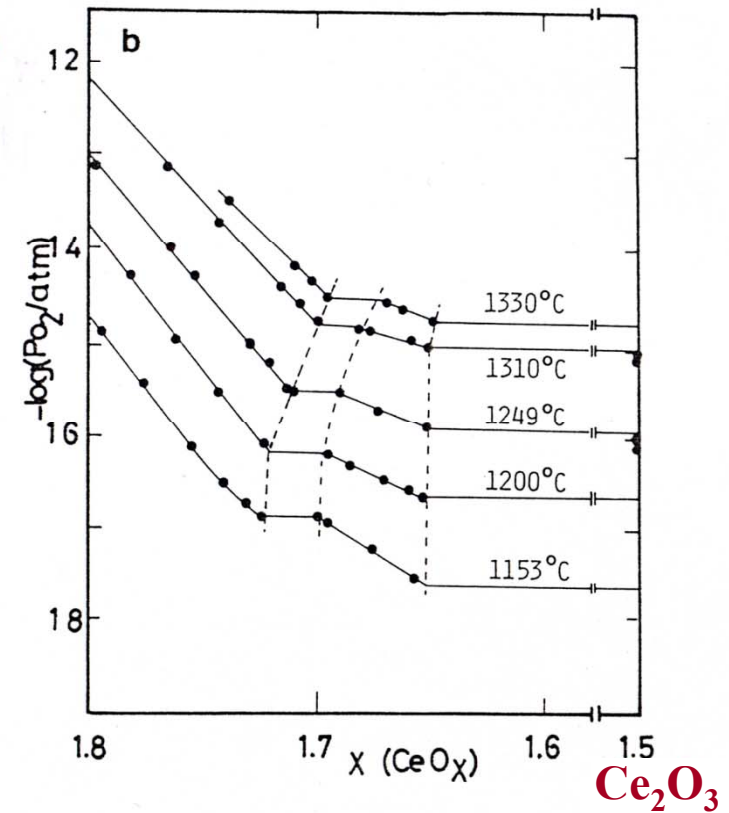
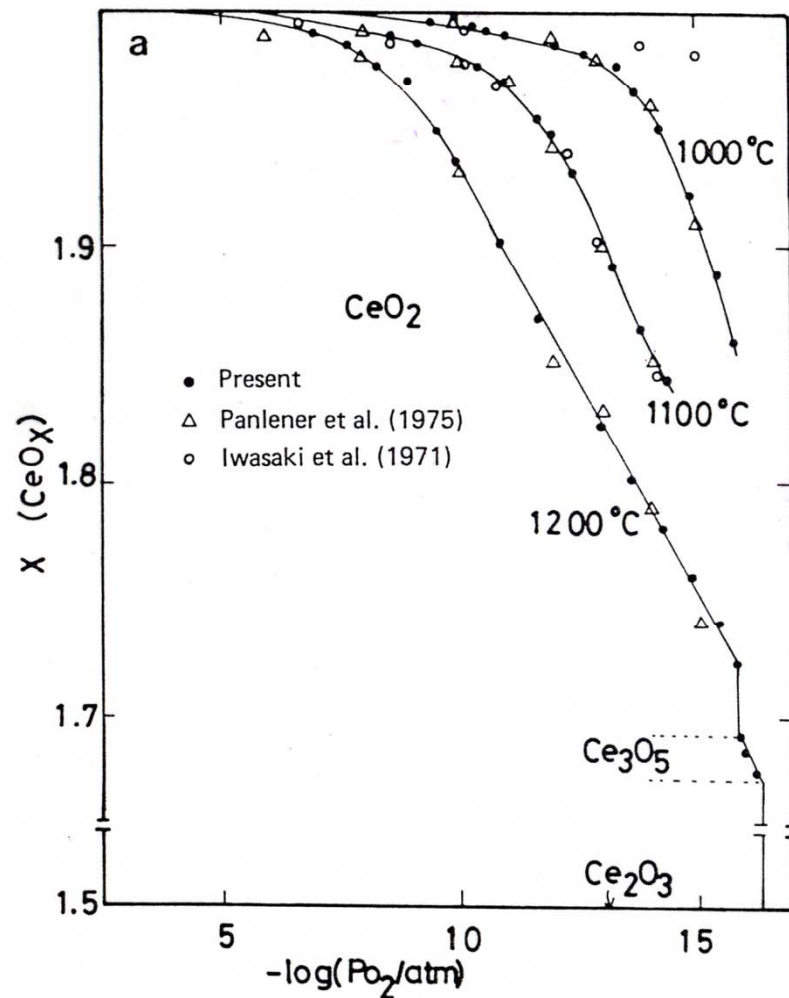
Cerium was reduced in air.

Zircon structure

This compd does not decompose (oxidize) even under $P_{\text{O}_2} > 10^3$ atm.

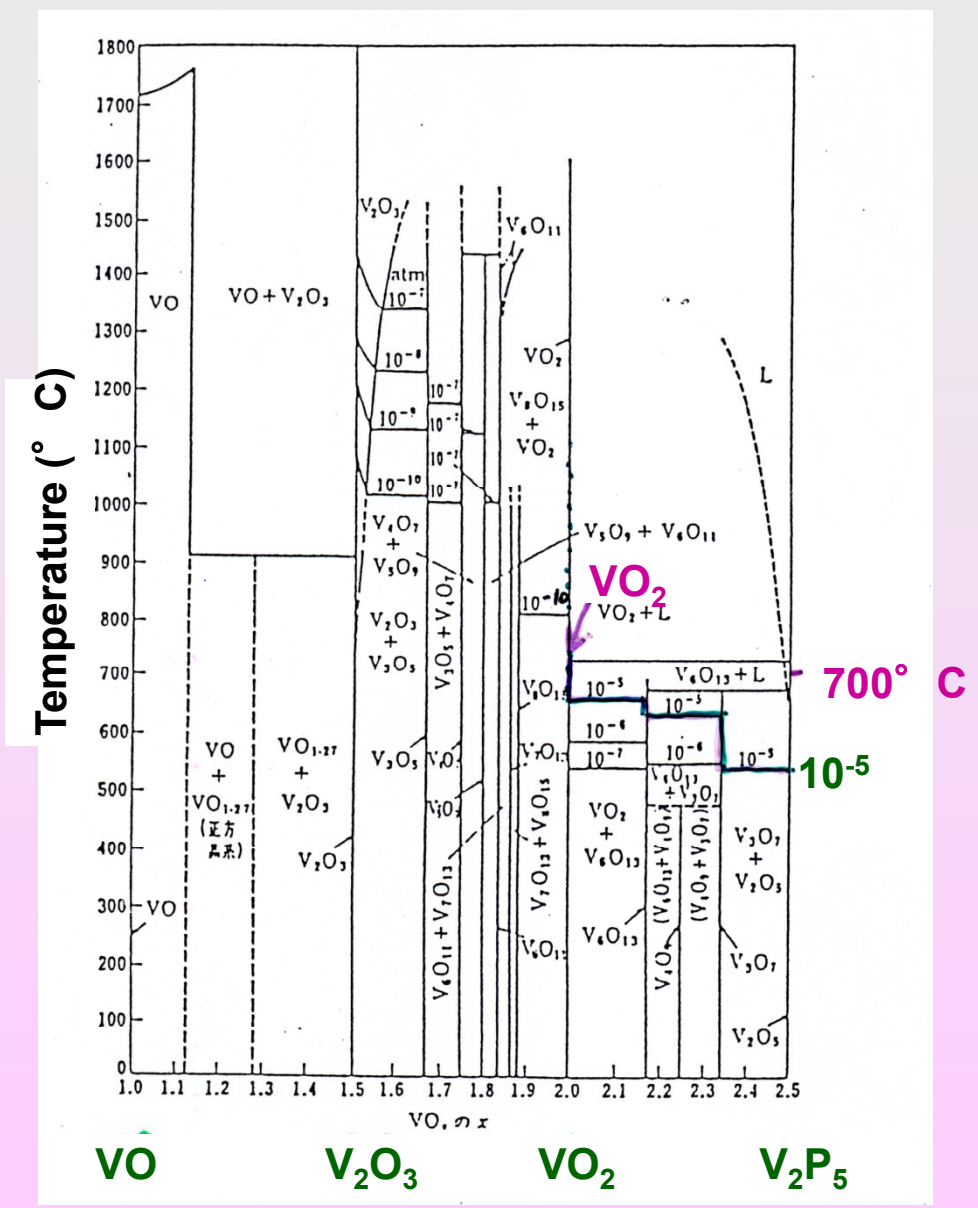
**TG-DTA curves for the reaction
In air ($P_{\text{O}_2} = 0.21$ atm)**

(Yoshimura '69)



The relationship between the oxygen partial pressure and the composition of Cerium oxide. (a) 1000, 1100, and 1200° C; 8b) 1153, 1200, 1249, 1310, and 1130° C

Kitayama, et al. ('85)
J. Solid State Chem.



VO - V₂O₅ phase diagram

A New Monoclinic Phase of Cerium Orthovanadate (CeVO_4)

Masahiro YOSHIMURA and Toshiyuki SATA

Research Laboratory of Engineering Materials, Tokyo Institute of Technology, Ookayama, Meguro-Ku, Tokyo

(Received June 2, 1969)

A new monoclinic phase of cerium orthovanadate, $\text{CeVO}_4(\text{H})$, was found during the course of oxidation of pseudo-perovskite CeVO_3 below 400°C . It has been confirmed to crystallize in the huttosite-type structure ($C_{2h}^2-P2_1/a$), that of LaVO_4 . The lattice parameters were determined to be:

$$a_0 = 6.98 \text{ \AA}, \quad b_0 = 7.22 \text{ \AA}, \quad c_0 = 6.76 \text{ \AA}, \quad \beta = 105^\circ 02', \quad V = 328 \text{ \AA}^3 \text{ and } Z = 4.$$

This phase was metastable, and exothermally transformed into a known stable CeVO_4 (tetragonal zircon-type, $D_{2d}^2-R_4/2am$) above 400°C , releasing a small amount of oxygen. From magnetic, chemical and thermogravimetric analyses, the valences of cerium ion and vanadium ion in $\text{CeVO}_4(\text{H})$ seem to be tripositive and pentapositive respectively, but V^{4+} ion is mixed in zircon-type CeVO_4 ; $\text{CeVO}_4(\text{Z})$.

Recent Papers on Valence Stability of Rare Earth Ions

- 1) “Understanding of the Valency of Rare Earths from First-principle Theory,” P. Strange, A. Svane, W. M. Temmermann, Z. Szotek, and H Winter, Nature 399 (24 June 1999) 756-758**
- 2) “Valence Stability of Lanthanide Ions in Inorganic Compounds,” P. Dorenbos, Chem. Mater. 17 (2005) 6452-6456**
- 3) “The Eu³⁺ Charge Transfer Energy and the Relation with the Band Gap of Compounds,” P. Dorenbos, J. Lumin, 111 (2005) 89-104**
- 4) “Stability of Rare Earth Oxychloride Phases: Bond Valence Study,” J. Hölsä, M. Lahtinen, M. Lastusaari, J. Valkonen, and J. Vijanen, J. Solid State Chem., 165 (2002) 48-55**
- 5) “Critical Materials Problems in Fuel Cells: SOFC’S,” H. Yokokawa, Oxford, April 02, 2007**

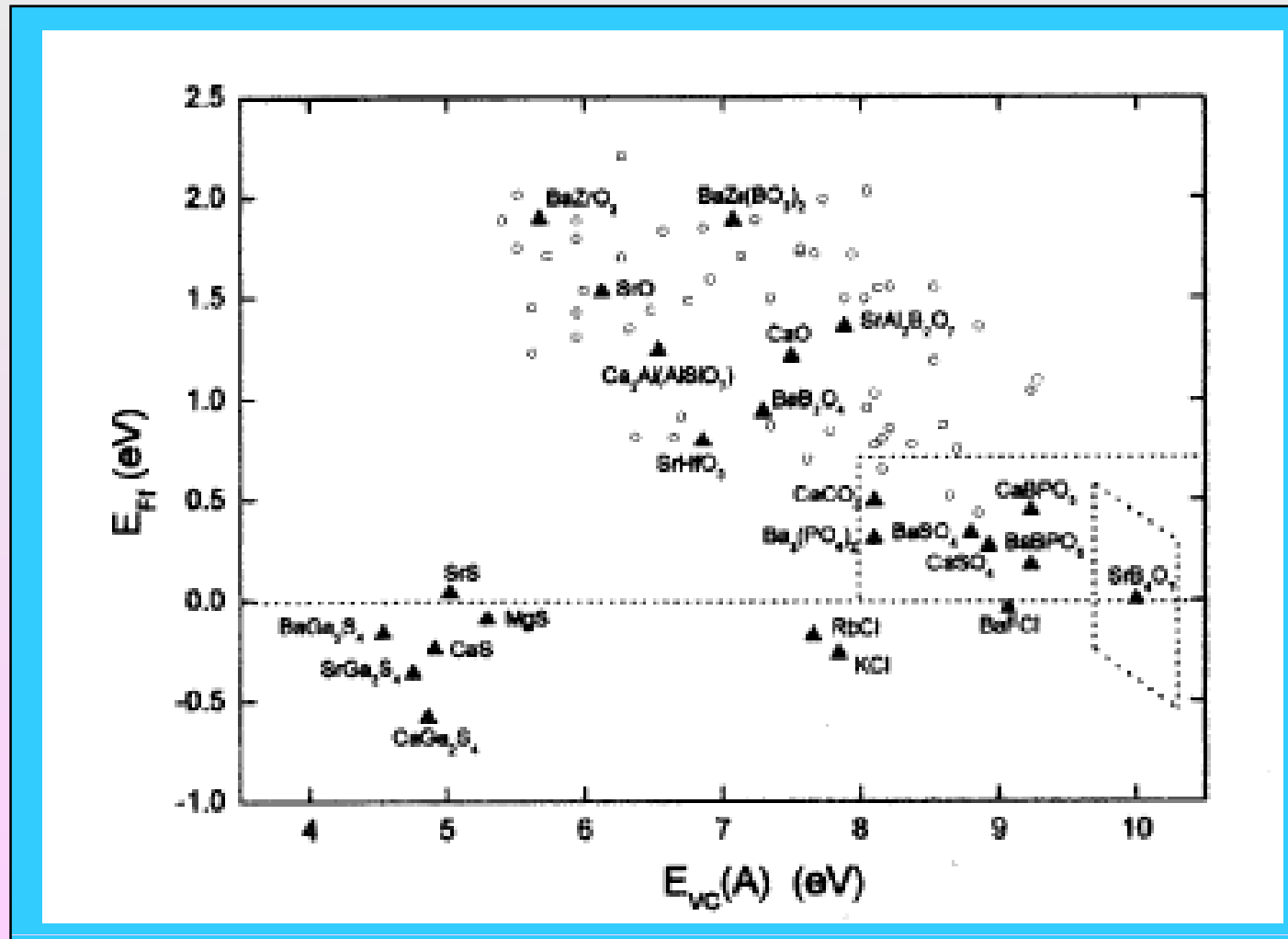


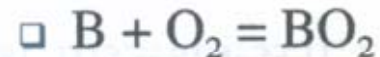
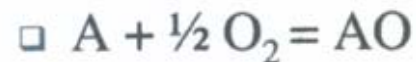
Figure 4. E_{Ff} for Eu^{2+} in oxide, chloride, and sulfide compounds. The solid triangle symbols pertain to Eu on Ba^{2+} , Sr^{2+} , Ca^{2+} , or Mg^{2+} sites and in addition to Eu in RbCl and KCl. The other data are the same data as in Figure 3 and pertain to Eu in trivalent rare earth oxide compounds. The box around data with $E_{Vc} > 8$ eV and $E_{Ff} < 0.7$ eV contains alkaline earth compounds in which Eu^{2+} can be obtained even under oxidizing conditions. P. Dorenbos, Chem. Mater. (2005) 17, 6452

Thermodynamics of acid-base and valence change in terms of valence stability and stabilization energy



Metal covalent molecule ionic crystal

■ Valence stability



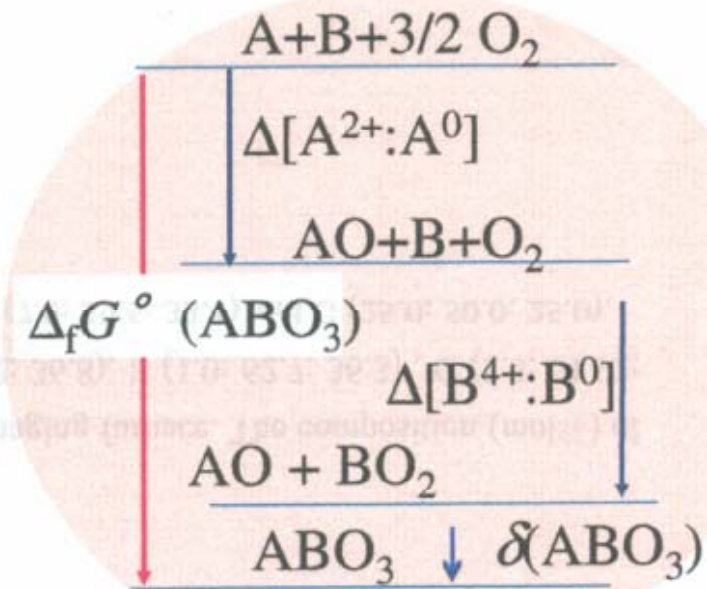
$$\Delta[A^{n+}:A^{m+}]$$

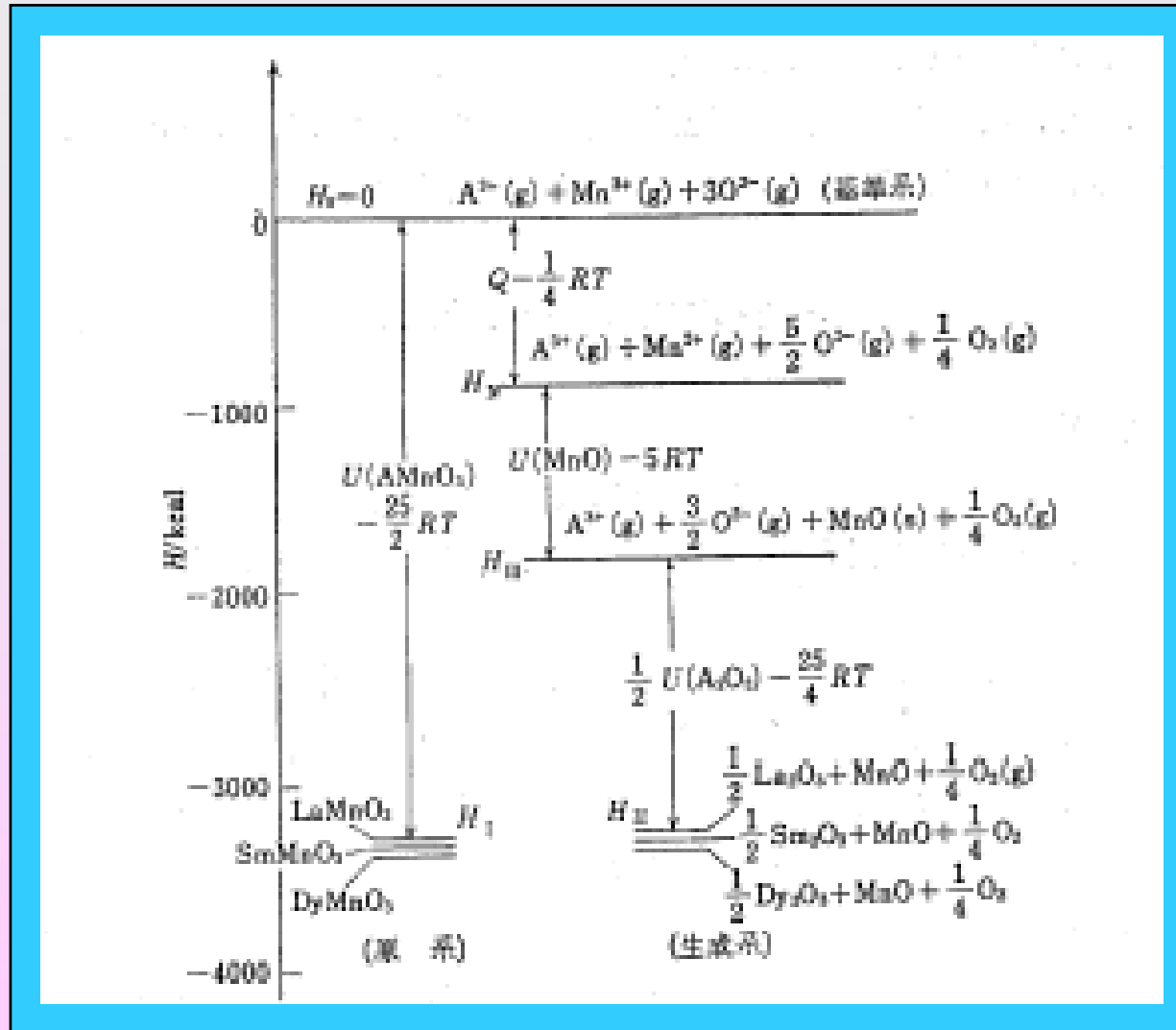
■ Stabilization energy



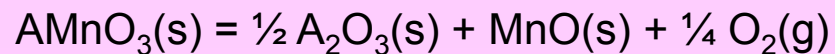
$$\delta(ABO_3)$$

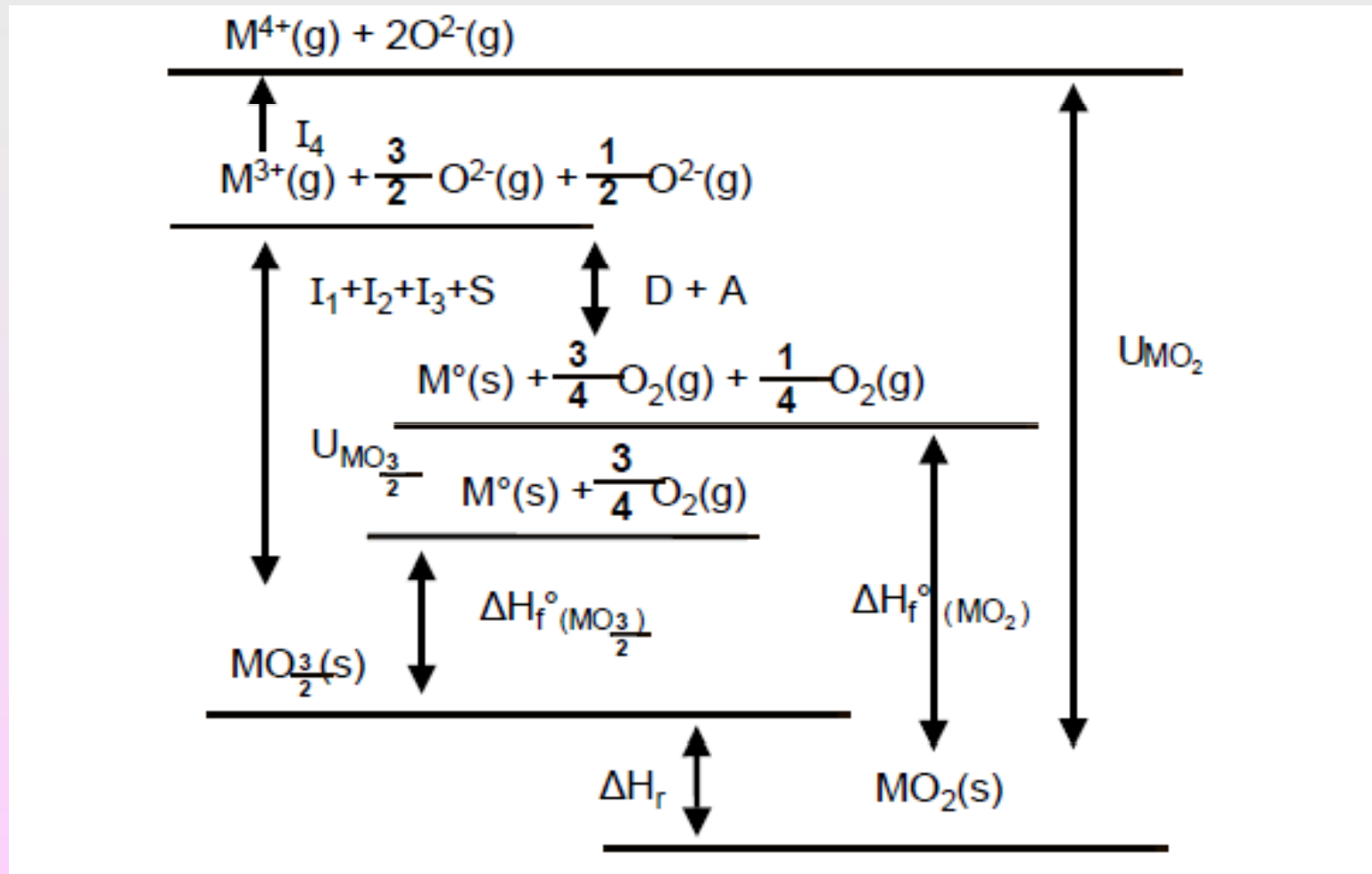
$$\Delta_f G^\circ (ABO_3) = \delta(ABO_3) - \Delta[A^{2+}:A^0] - \Delta[B^{4+}:B^0]$$





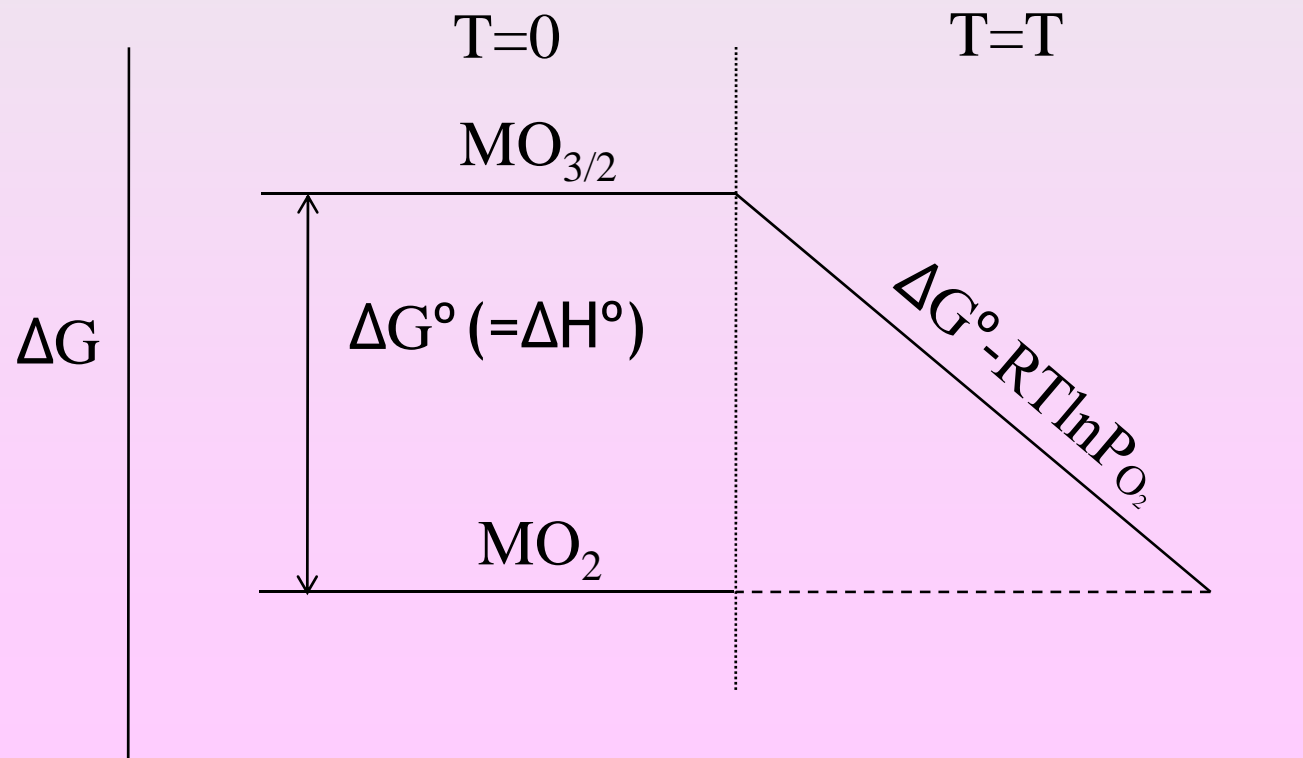
Enthalpy Diagram for the reduction of rare earth (A) Manganates; T. Nakamura (1985)





Energy Diagram for the Reaction: $\text{MO}_3(\text{s}) + \frac{1}{4}\text{O}_2(\text{g}) \rightarrow \text{MO}_2(\text{s})$ 【 ΔG°_r 】

U: Lattice energy, D: Dissociation energy, A: Electron affinity
 H_f° : Standard formation enthalpy, I_4 : 4th Ionization energy



Lattice energy (U) is also given by

$$U = Ne^2 \sum_j \frac{q_j p_j \phi_j}{2k}$$

N: Avogadro No.

q_j: Valency of j-ion

sublattice

φ_j: Lattice-site potential of j-ion

p_j: Occurrence of j-ion in the unit cell

k: Molecular No. in the unit cell

$$U = -331.98 \left(\frac{M_a}{a} \right)$$

[kcal / mol] for φ [Å⁻¹]

$$M_a = -a \sum_j \frac{q_j p_j \phi_j}{2k}$$

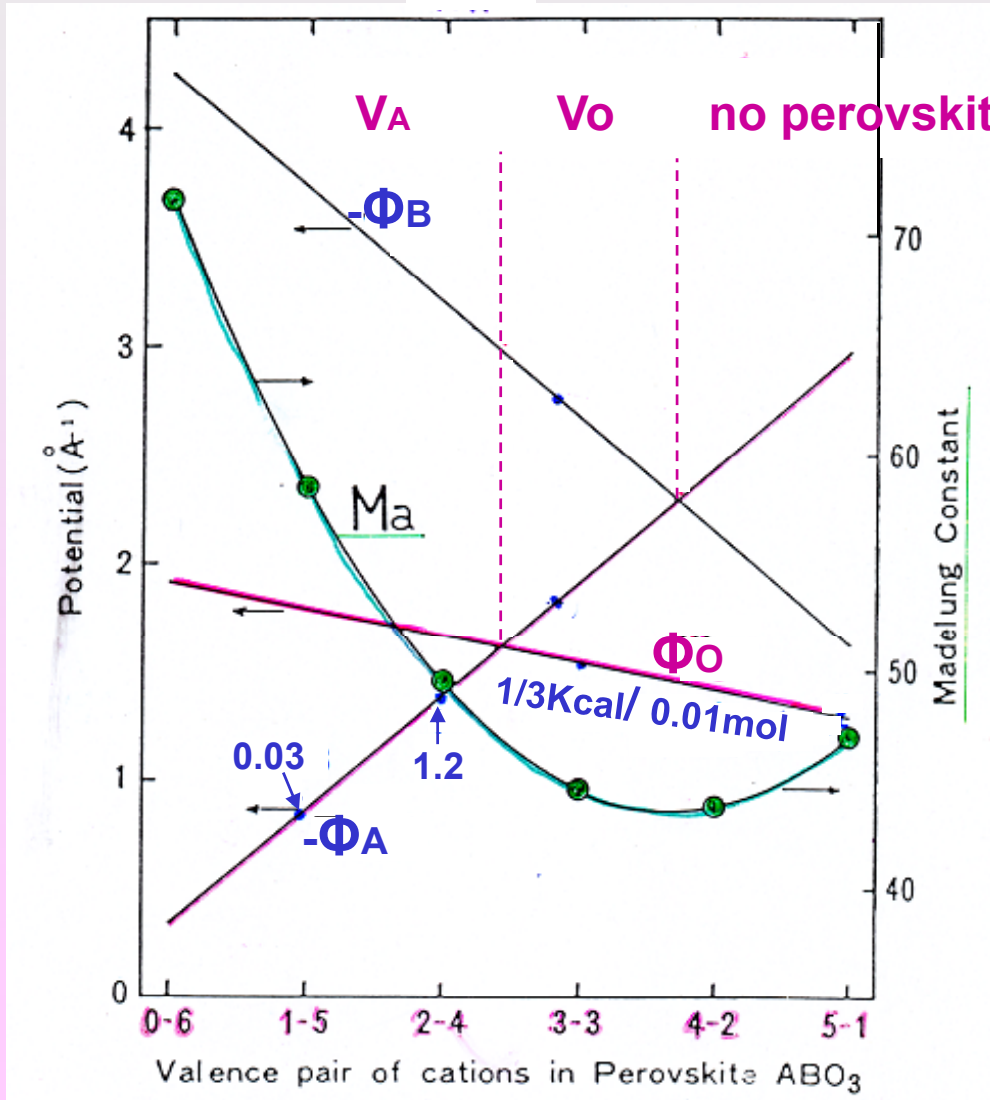
Madelung Lattice Site Potentials in Europium Containing Oxide

Compound	structure	Lattice site potential			
		ϕ_{Eu}	ϕ_M	ϕ_O	
Eu ²⁺	EuO	NaCl	-1.359	1.359	
	EuTiO ₃	Perovskite	-1.380	-3.171	1.653
	Eu ₃ O ₄	Eu ₃ O ₄	-1.377	-2.076/-2.088	1.423~1.457
Eu ³⁺	Eu ₂ O ₃	B-type	-2.081~-2.107	1.432~1.507	
	EuFeO ₃	Perovskite	-2.051	-2.500	1.576/1.602
	EuMnO ₃	Perovskite	-2.055	-2.495	1.574/1.633
	EuScO ₃	Perovskite	-2.038	-2.382	1.543/1.557
	Eu ₂ Ti ₂ O ₇	Pyrochlore	-2.167	-3.100	1.523/1.640
	EuPO ₄	Zircon	-2.116	-4.160	1.882~1.970

Madelung Lattice Site Potentials in Cerium Containing Oxide

Compound	structure	Lattice site potential			
		ϕ_{Ce}	ϕ_{M}	ϕ_{O}	
Ce ³⁺	Ce ₂ O ₃	A-type	-2.036	1.400/1.405	
	CeAlO ₃	Perovskite	-1.965	-2.738	1.578/1.582
	CeCrO ₃	Perovskite	-1.908	-2.659	1.535
	CeGaO ₃	Perovskite	-1.915	-2.669	1.540/1.547
	CeVO ₄	Zircon	-2.103	-3.697	1.803
	CeTaO ₄	d-Sheelite	-2.136	-3.595	1.52~1.79
	LiCeO ₂	NaFeO ₂	-1.962	-1.080	1.438/1.474
	CeTa ₃ O ₉	Layered Perovskite	-2.126	-3.646/-3.660	1.679~1.808
Ce ⁴⁺	CeO ₂	Fluorite	-2.797	1.504	
	BaCeO ₃	Perovskite	-2.816	-1.226	1.468
	SrCeO ₃	Perovskite	-2.893	-1.256	1.503

$ \Phi_B $	$ \Phi_B $
V	V
$ \Phi_O $	$ \Phi_A $
V	V
$ \Phi_A $	$ \Phi_O $



Site self-potential and Madelung constant
For ideal Perovskite lattice,
 $a = 3.881 \text{ \AA}$

$$Ma = -a \sum \frac{q_i p_i \phi_i}{2k}$$

$$U = 332(Ma/a)$$

Perovskite (ABO₃) lattice

$$U = (1/2) Ne^2(q_A\phi_A + q_B\phi_B + 3q_O\phi_O)$$

$$p_A = p_B = 1, \quad p_O = 3, \quad k = 1$$

$$q_A + q_B + 3q_O = 0$$

charge neutrality

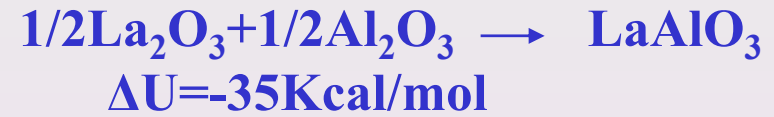
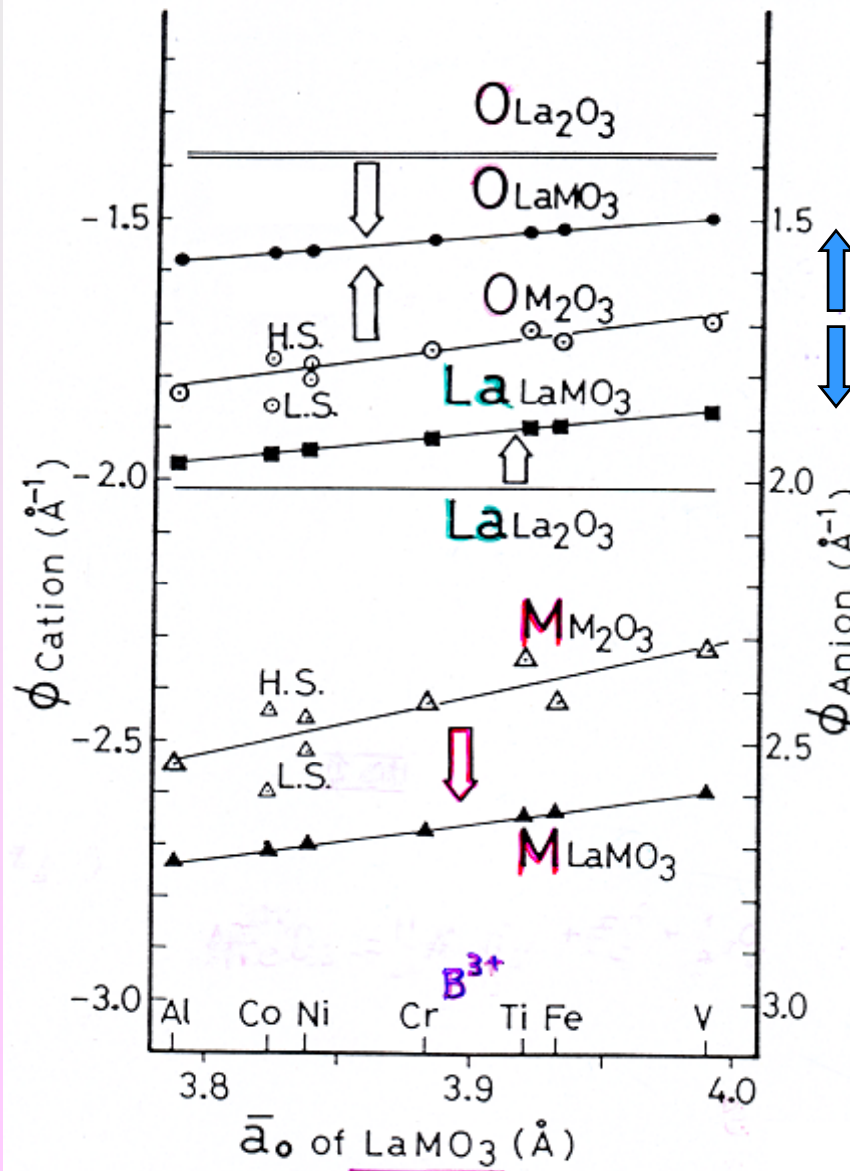
Ma: Madelung constant for the lattice parameter of unit cell (a)

$$U = Ne^2 \sum \frac{qp^{\dagger}}{2k}$$

(1) $|\phi_B| > |\phi_A|$

(2) ϕ_O decrease with valency-pair from 0-6 to 3-3.

(3) Ma decrease with valency-pair from 0-6 to 3-3.



Loss

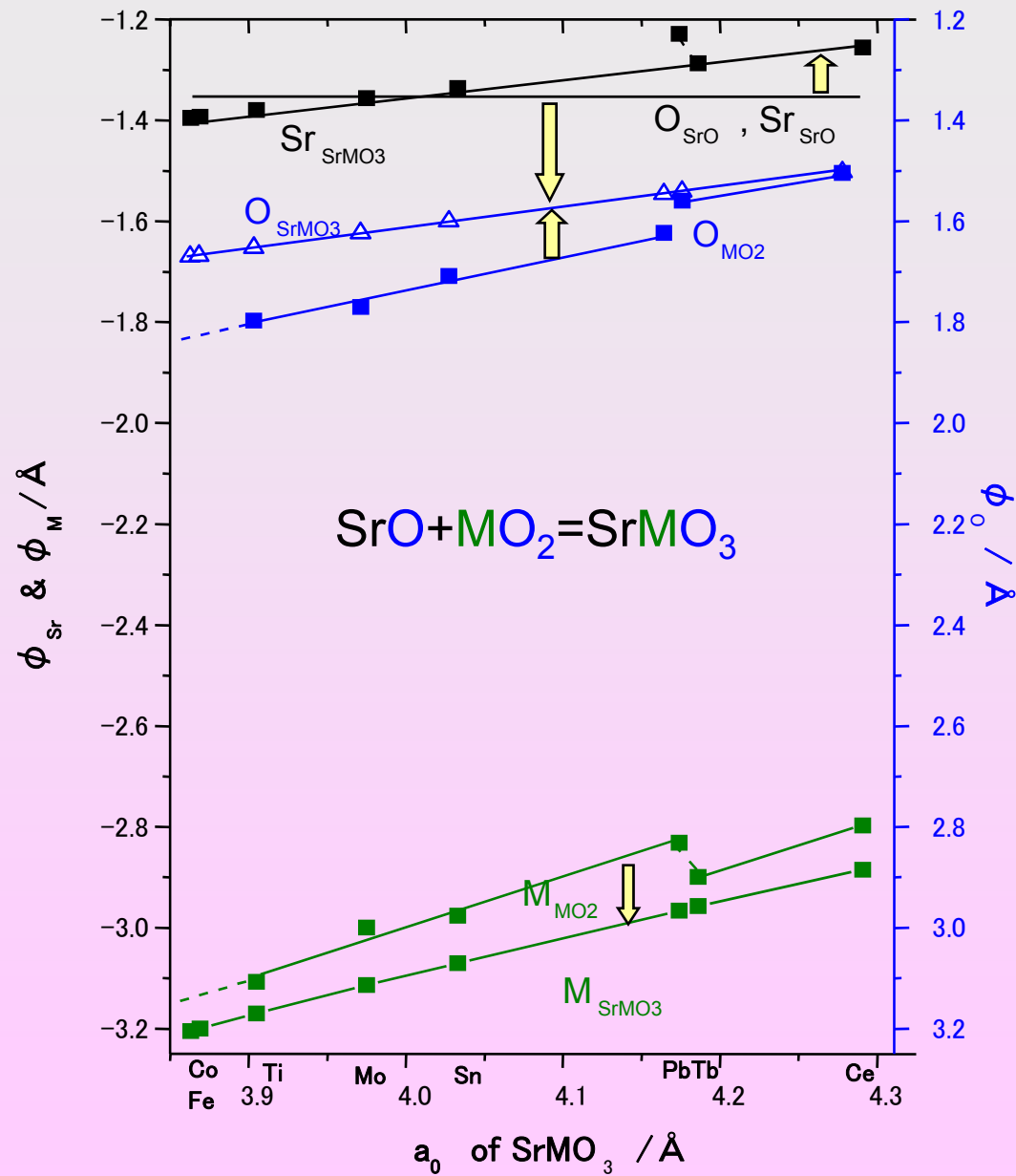
Gain

Site self potential change for the formation of LaMO_3 from $\text{La}_2\text{O}_3 + \text{M}_2\text{O}_3$

Φ for Co_2O_3 and Ni_2O_3 in High-Spin & Low-Spin states are estimated from ionic radii.

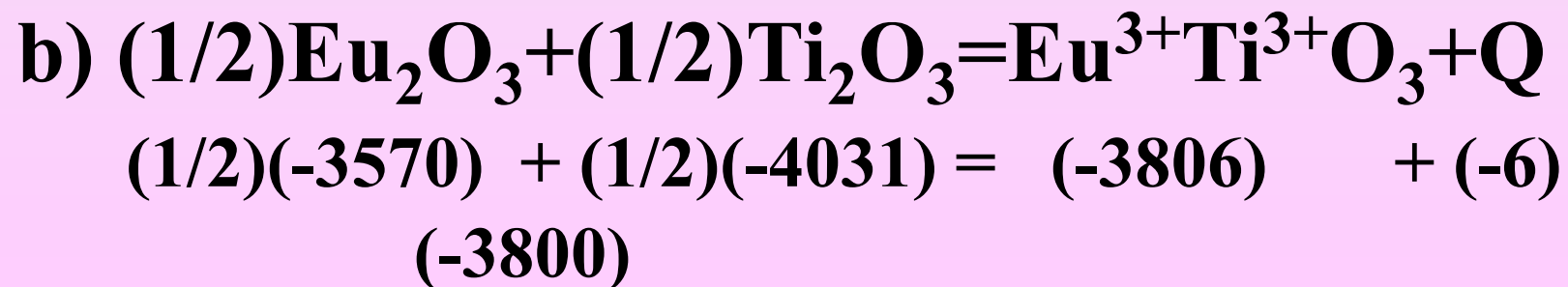
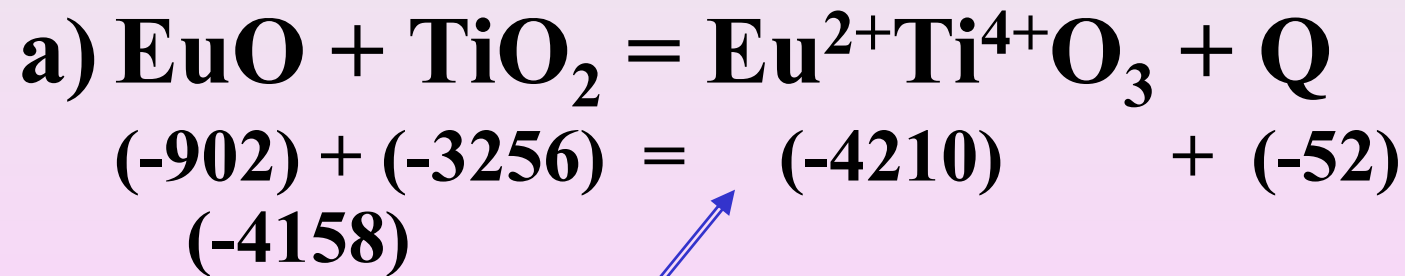
Co^{3+} , Ni^{3+} etc. stabilized by strong Φ_M

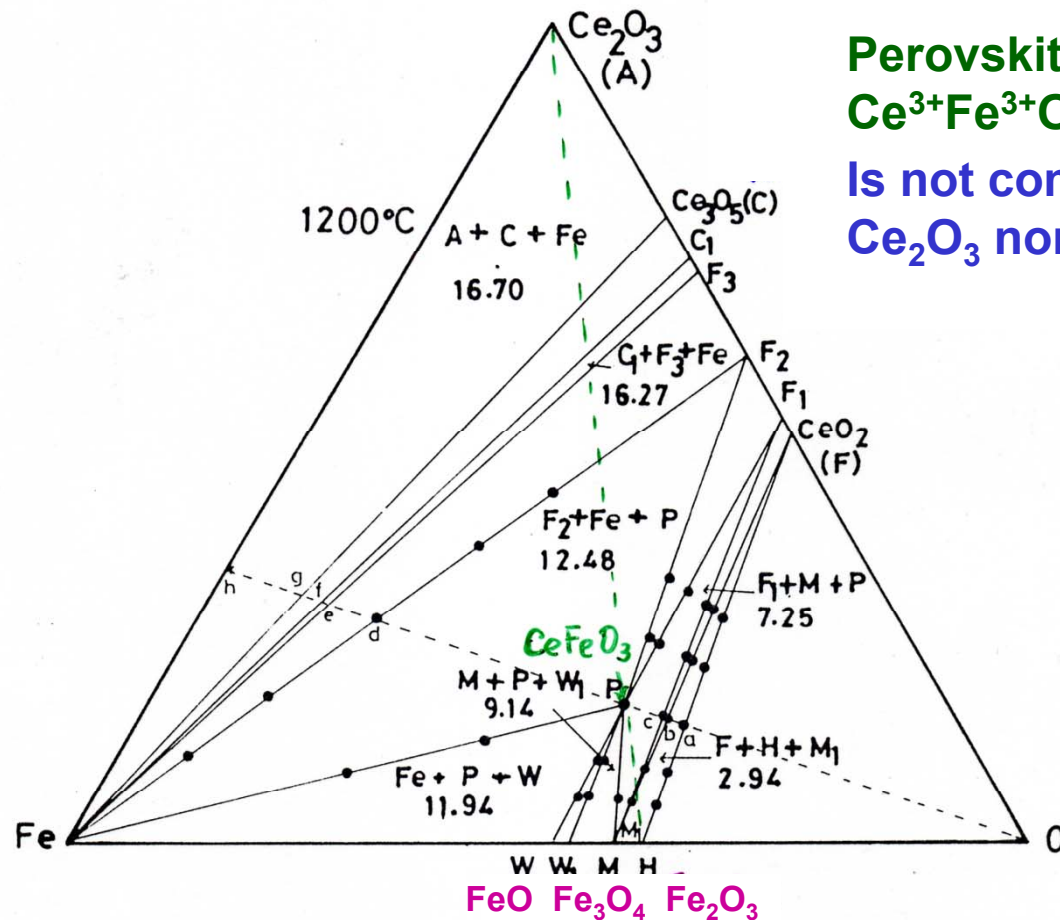
B-ion has a 6-coordination in LaMO_3 as well as in M_2O_3 (MO_2 , MO ,



Change of Lattice Site Potentials of Every Site in the Reaction
 $\text{SrO} + \text{MO}_2 = \text{SrMO}_3$

Lattice energy change in the formation of EuTiO_3





Perovskite
 $\text{Ce}^{3+}\text{Fe}^{3+}\text{O}_3$
 Is not compatible with
 Ce_2O_3 nor Fe_2O_3 !!

FIG. 5. The phase equilibria in the Ce_2O_3 -Fe-O system at 1200°C . Numerical values in the three solid phases regions are the equilibrium oxygen partial pressure in $-\log P_{\text{O}_2}$. Symbols are the same as those in Table I.

KITAYAMA ET AL ('85)

Summary

(1) Valence stability is different in ternary systems from binary systems.

X-P_{O2} - T diagram in RO_x

X-y-P_{O2} - T diagram in RM_yO_x

(2) Valence stability is directly related to electrostatic lattice-site potential (ϕ),

$$U = Ne^2 \sum \frac{pq\phi}{2k} \Rightarrow 331.98 \sum \frac{pq\phi}{2k} \quad [\text{kcal/mol}] \text{ for } \phi [\text{\AA}]$$

(3) for example:

$\phi \approx 1.36-1.38$ for Eu²⁺, $\phi \approx 2.04-2.17$ for Eu³⁺

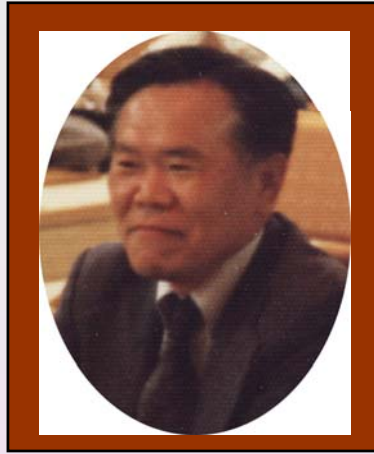
$\phi \approx 1.8-2.1$ for Ce³⁺, $\phi \approx 2.8-2.9$ for Ce⁴⁺

(4) In perovskite (ABO₃) lattice, High valency state in B-site & difficult defect formation in B-site due to strong ϕ_B potential.

(5) CeO₂ may be reduced during the reaction with MO_x when M is high valent, small ion and MO_x-rich part.



Thanking



Prof. Sata



Prof. Somiya



Colleagues