Database development for the HotVeGas project

Elena Yazhenskikh[1], Tatjana Jantzen[2], Dmitry Sergeev[1], Klaus Hack[2], Moritz to Baben[2], Michael Müller[1]

[1] - Forschungszentrum Jülich, Institute of Energy and Climate Research (IEK-2, Microstructure and properties of materials), Germany

[2] - GTT-Technologies, Germany

GTT Users' Meeting 2020, June 24 - June 25, Herzogenrath, Germany

Oxide database

HotVeGas Project

HOTVEGAS
Hochtemperaturvergasung und Gasreinigung

Basic experiments and thermochemical modelling

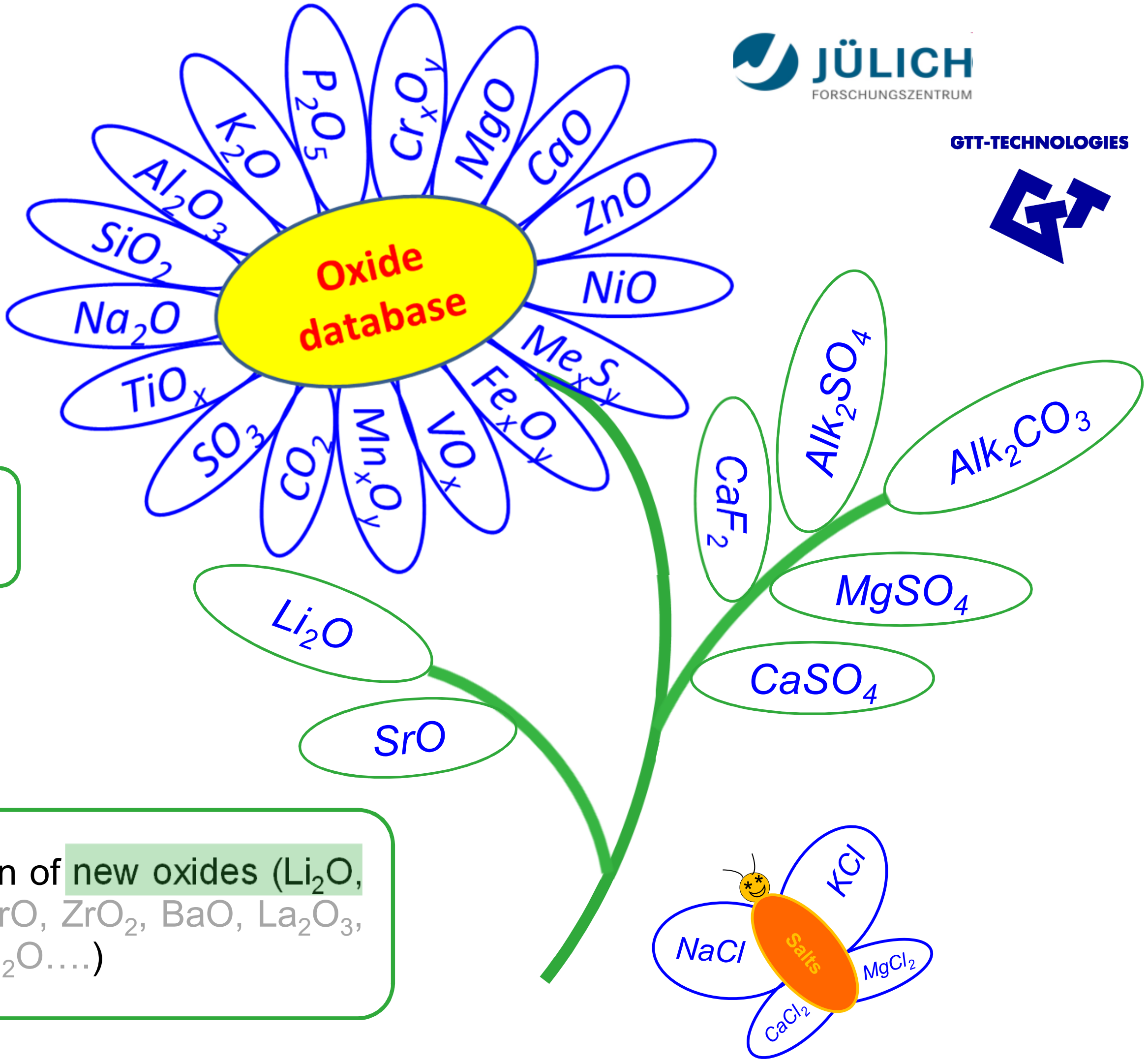
↓ Experiments

(slag, membranes, trace elements, etc.; with TA, XRD, KEMS, MBMS, Visco, etc.)

↓ Database development

Work on various sub-systems for the purpose of database` completeness (SO_3, TiO_2, V_2O_5, NiO, P_2O_5)

Addition of new oxides (Li_2O, CO_2, SrO, ZrO_2, BaO, La_2O_3, WO_3, H_2O….)



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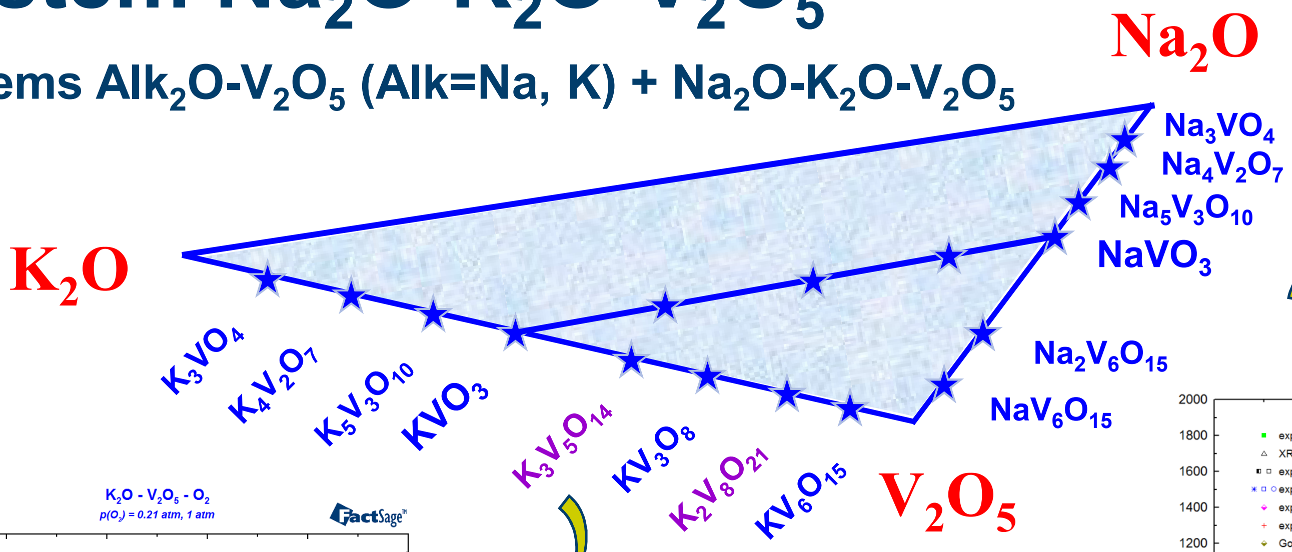
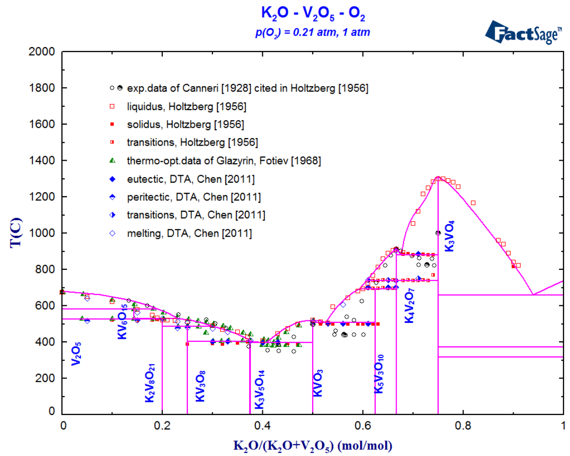
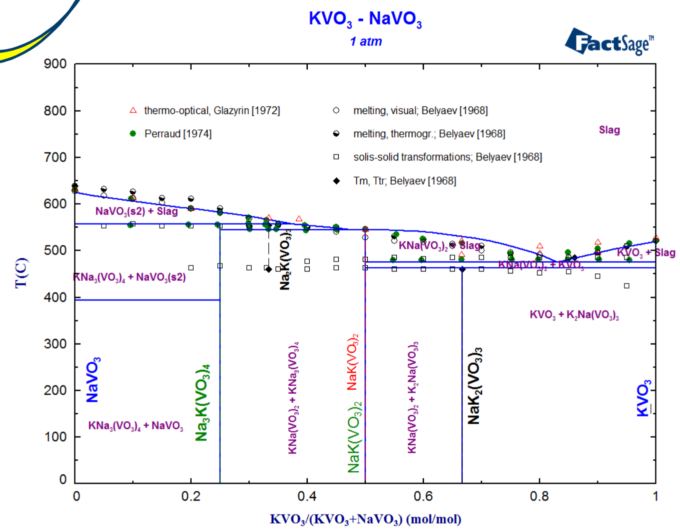
GTT-TECHNOLOGIES

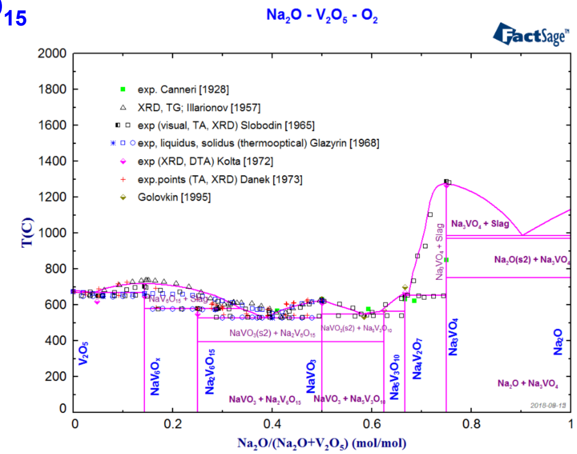
System Na_2O-K_2O-V_2O_5

Systems Alk_2O-V_2O_5 (Alk=Na, K) + Na_2O-K_2O-V_2O_5









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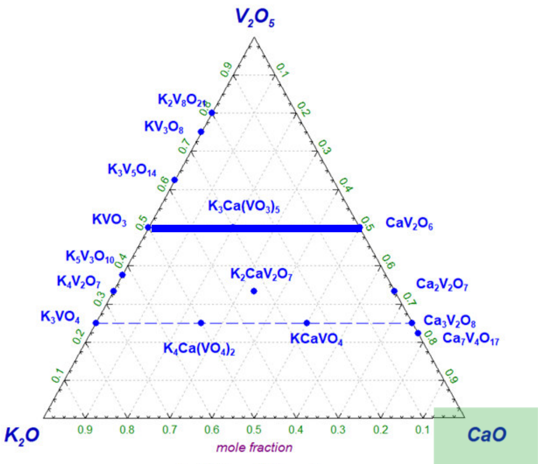
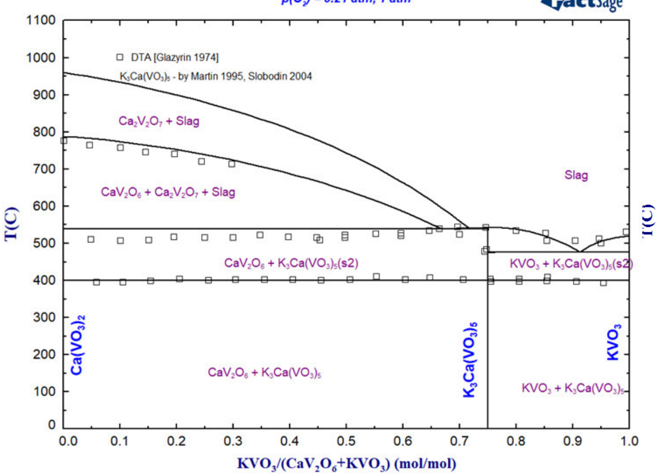
System MeO-K_2O-V_2O_5

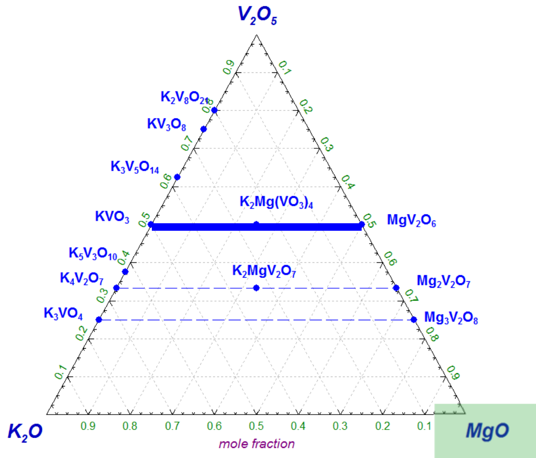
Me=Ca, Mg, Zn

- ✓ *Ternary vanadates are included*
- ✓ *No ternary associates in the slag*
- ✓ *Isopleths are considered*

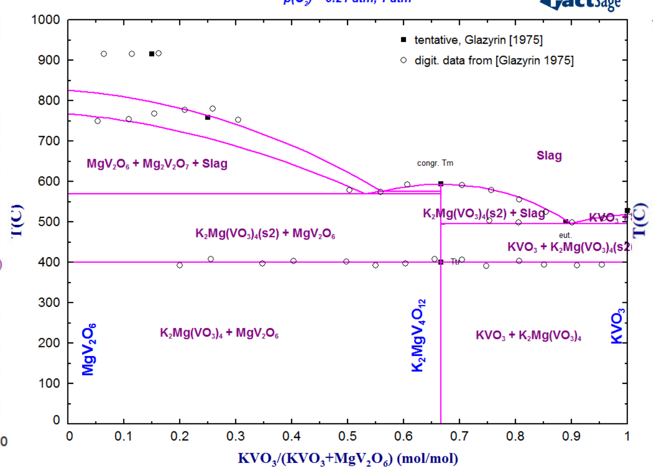


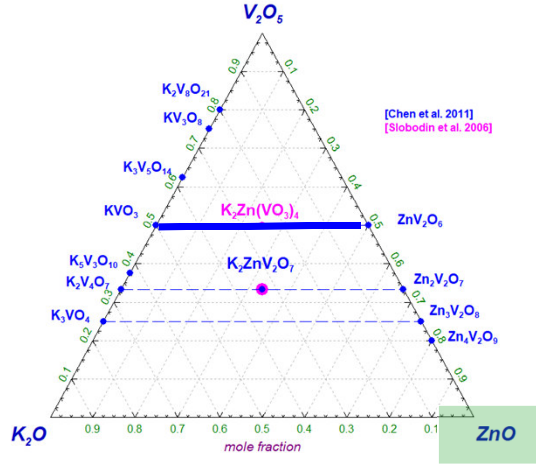
CaV2O6 - KVO3 - O2
p(O2) = 0.21 atm, 1 atm



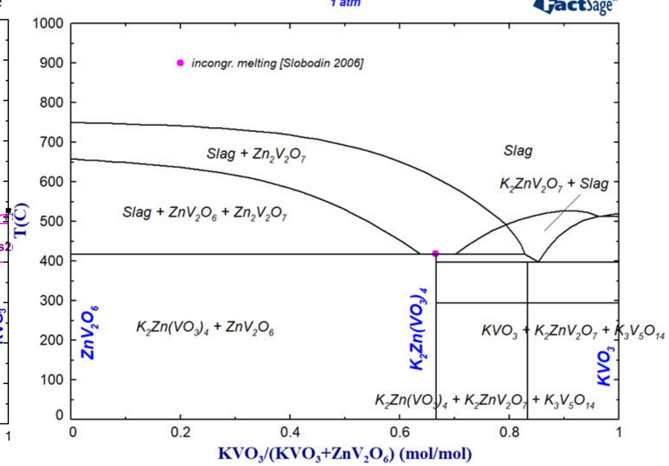


KVO3 - MgV2O6 - O2
p(O2) = 0.21 atm, 1 atm





KVO3 - ZnV2O6
1 atm



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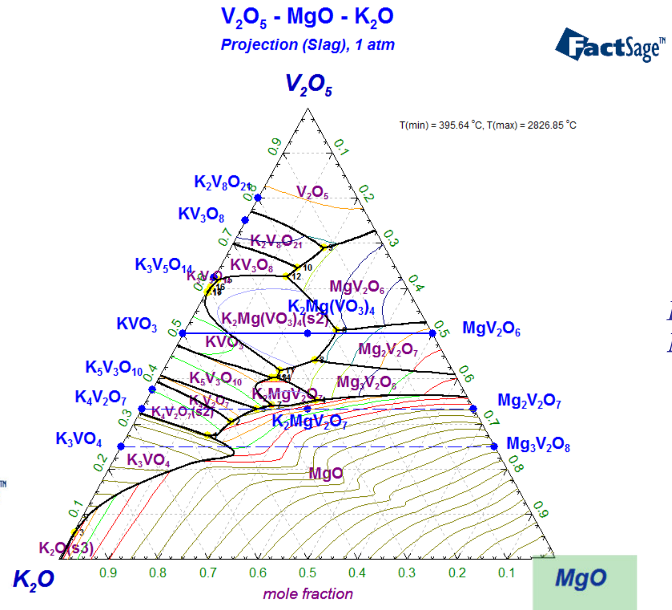
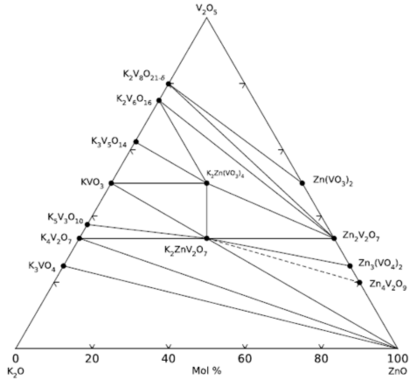
System MeO-K_2O-V_2O_5

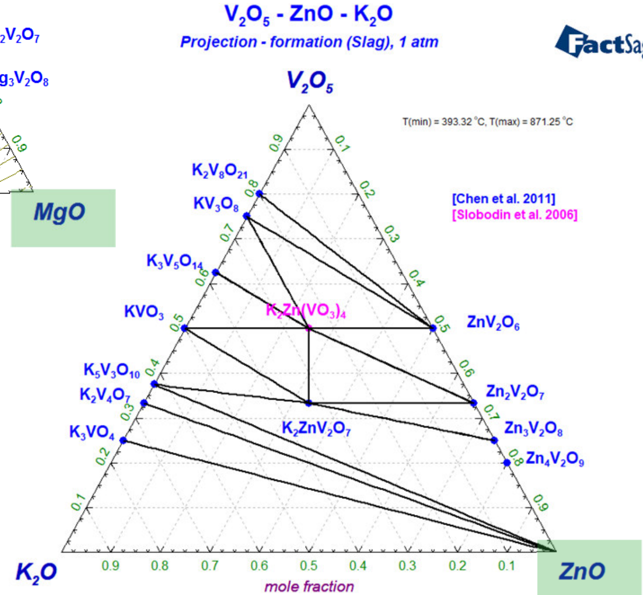
Liquidus surface

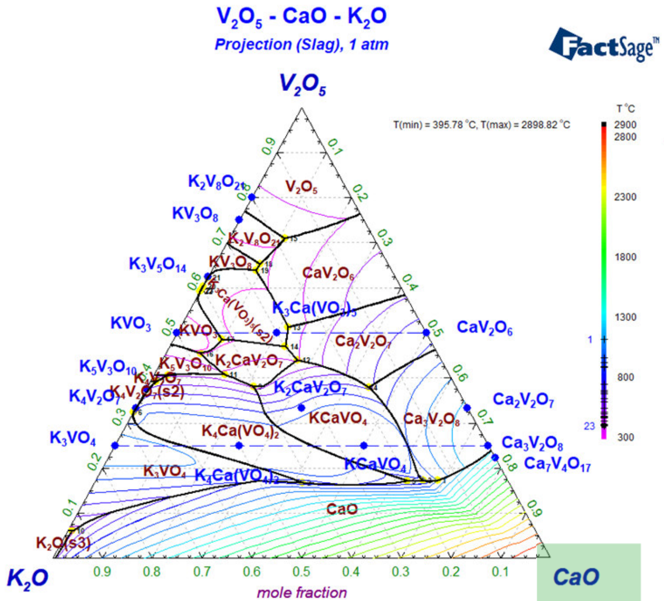
- ✓ *Ternary vanadates are included*
- ✓ *No ternary associates in the slag*
- ✓ *Isopleths are considered*
- ✓ *Liquidus surface/subsolidus is proposed*





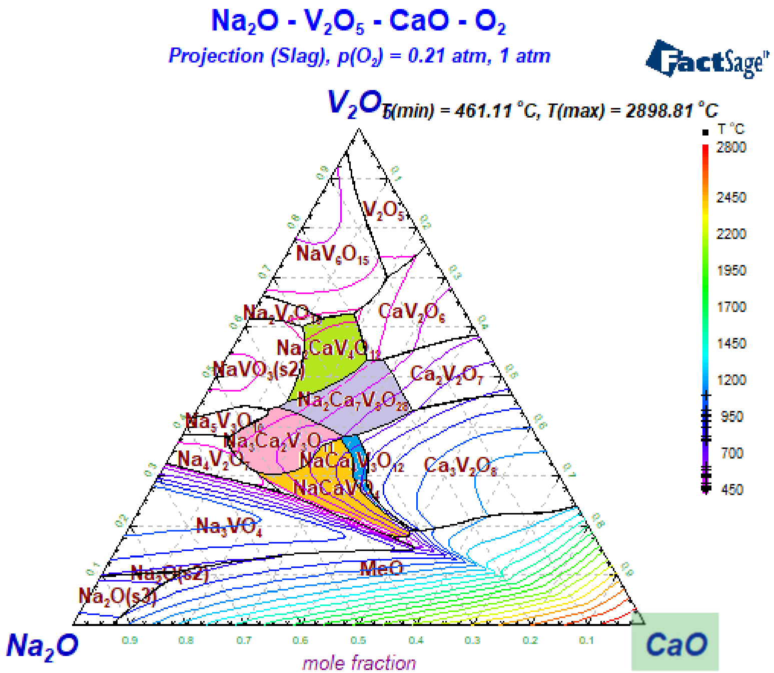
B. V. Slobodin and L. L. Surat, Zh. Neorg. Khim., 51 [9] 1435-1438 (2006)



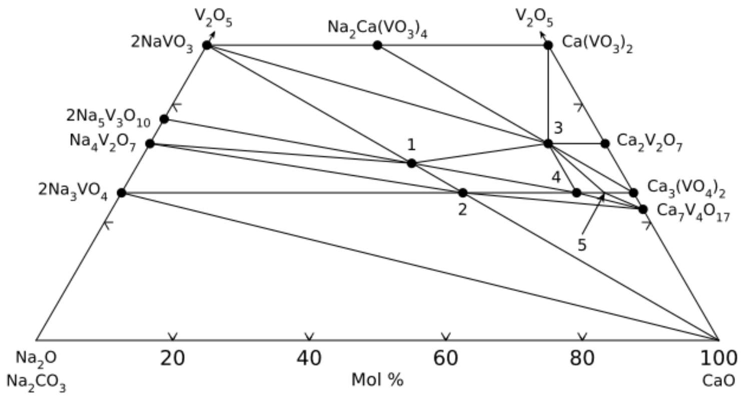


System CaO-Na_2O-V_2O_5

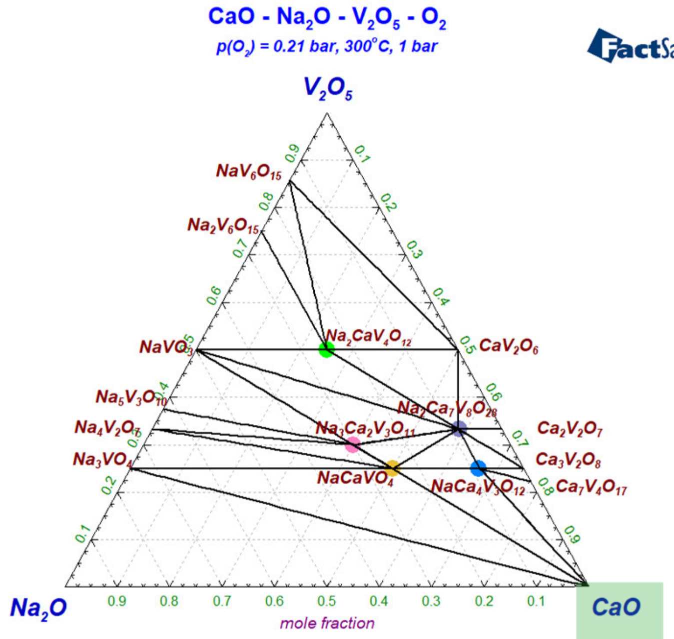
MeO_x-Na_2O-V_2O_5 (Me=Ca, Fe, Zn)



Phase	Experiment	Calc.
$Na_2CaV_4O_{12}$	570[Slobodin 2000] 550[Krasnenko1987]	569
$Na_3Ca_2V_3O_{11}$		807
$NaCaVO_4$	~1000	934
$Na_2Ca_7V_8O_{28}$	~880[Krasnenko1987]	888
$NaCa_4V_3O_{12}$	~1000	999

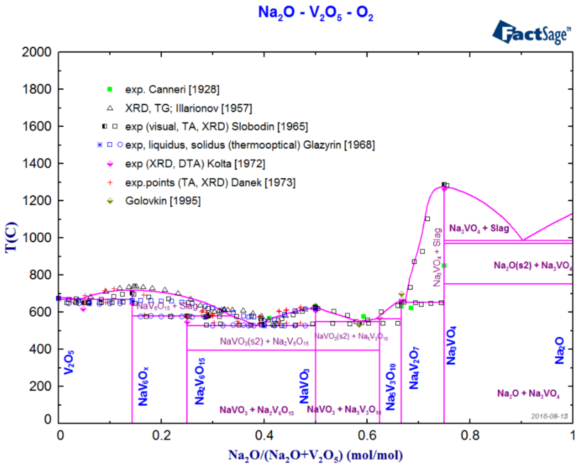


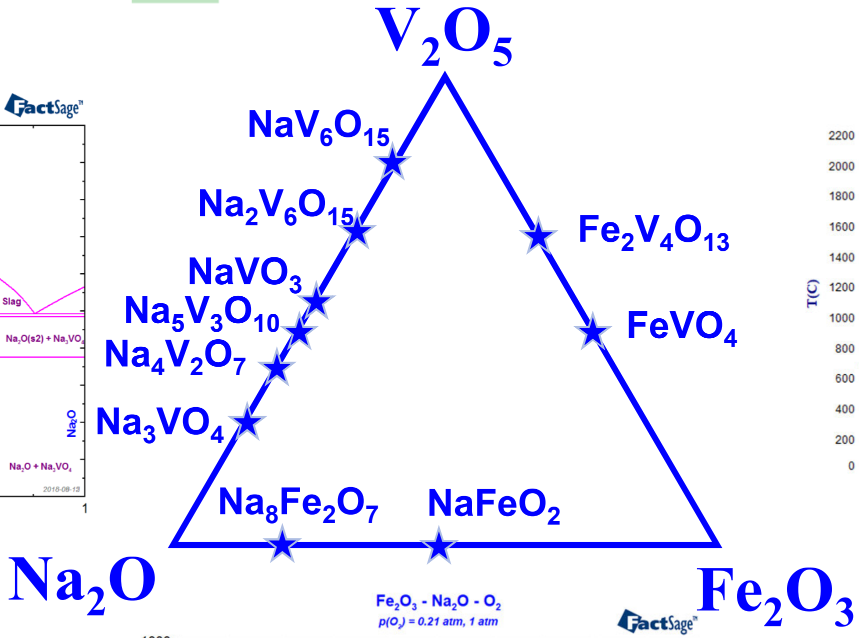
B. V. Slobodin, L. V. Kristallov, Zh. Neorg. Khim., 45 [3] 548-551 (2000); Russ. J. Inorg. Chem. (Engl. Transl.), 45 [3] 482-485 (2000).

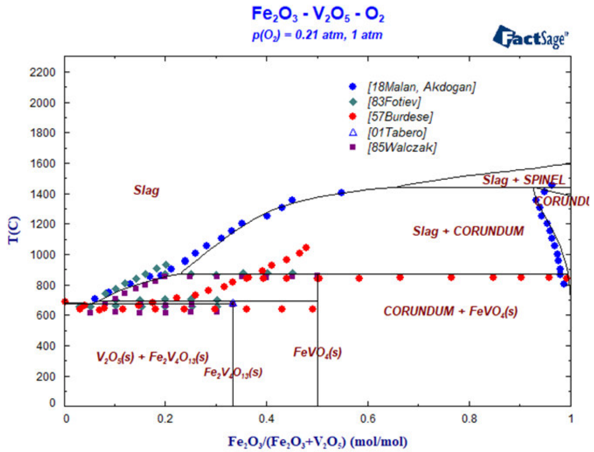


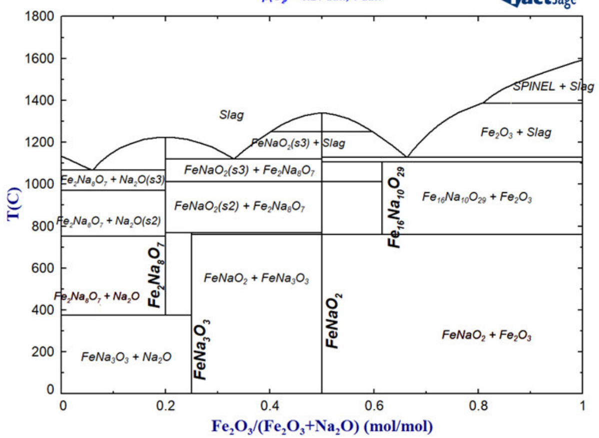
System Fe_2O_3-Na_2O-V_2O_5

MeO_x-Na_2O-V_2O_5 (Me=Ca, Fe, Zn)









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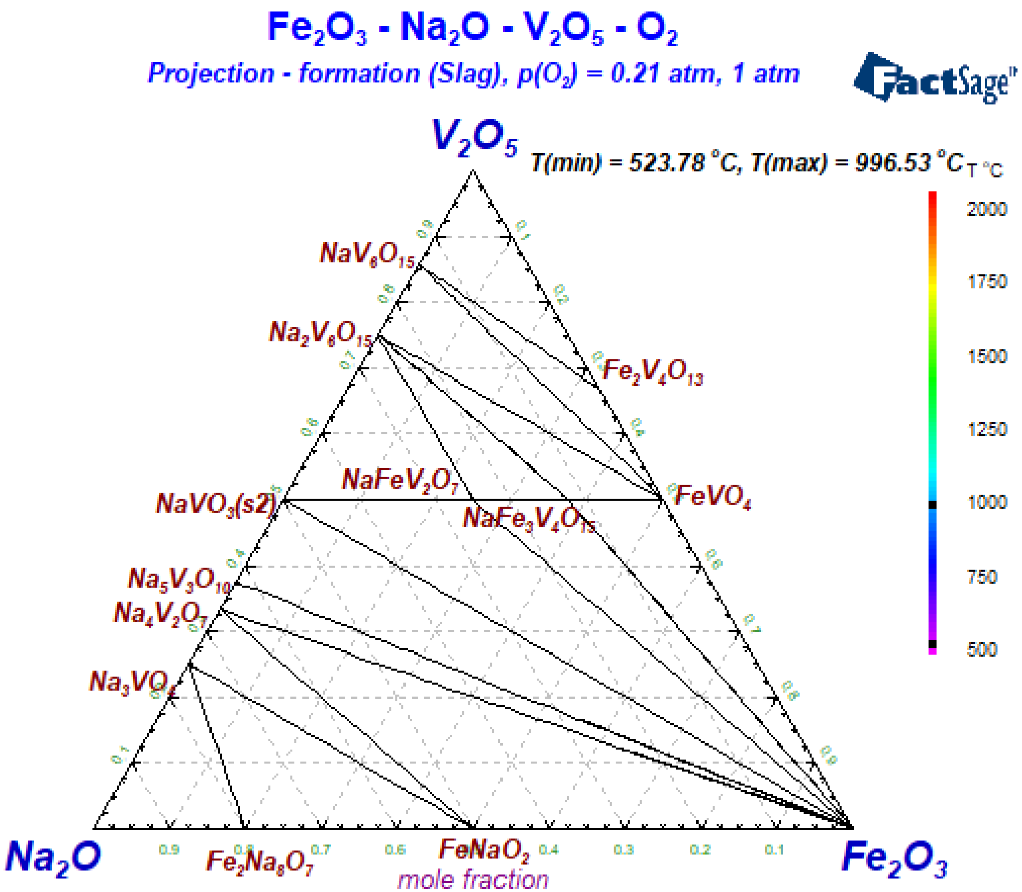
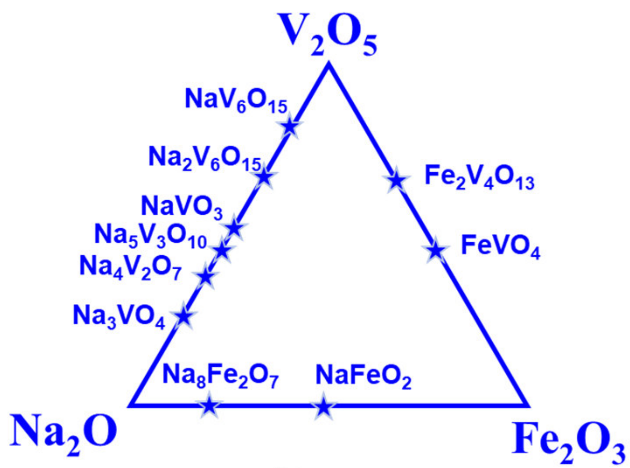
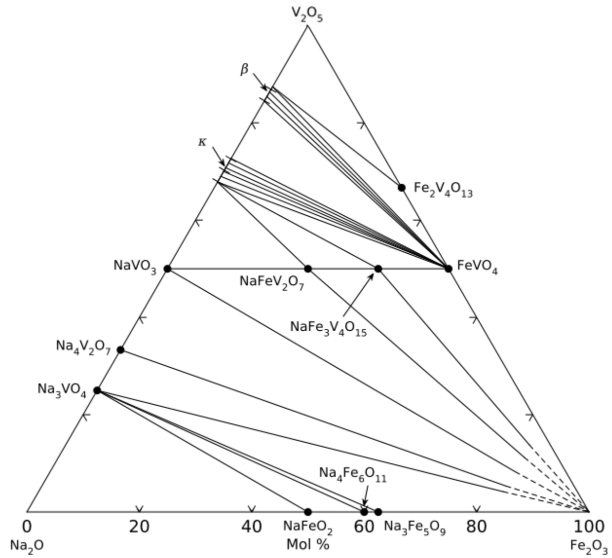
System Fe_2O_3-Na_2O-V_2O_5

Subsolidus



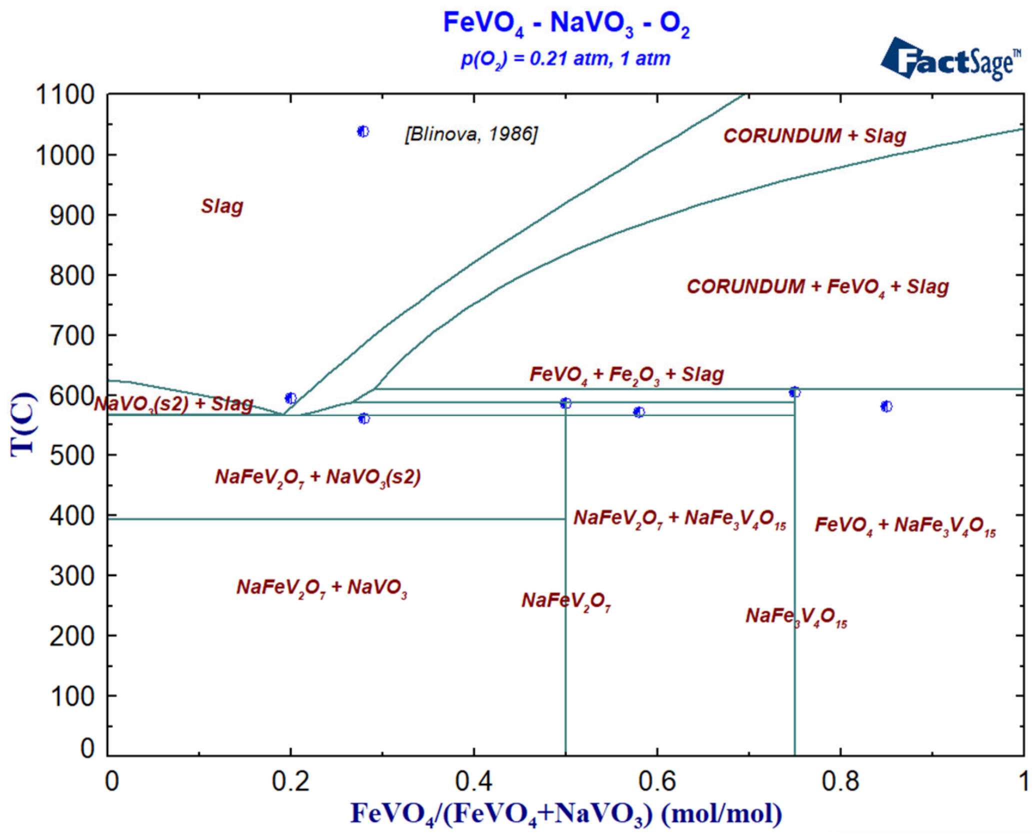


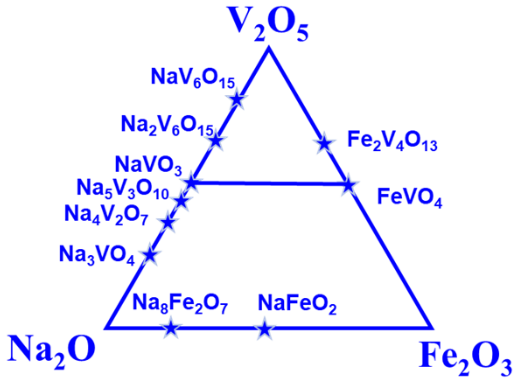


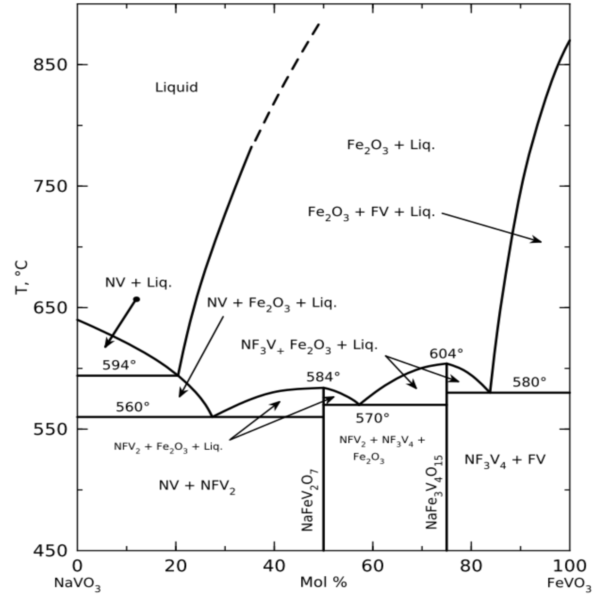
B. V. Slobodin, S. F. Blinova, and A. A. Fotiev, Zh. Neorg. Khim., 23 [10] 2815-2818 (1978).

System Fe_2O_3-Na_2O-V_2O_5

Sub-system $NaVO_3$-$FeVO_4$



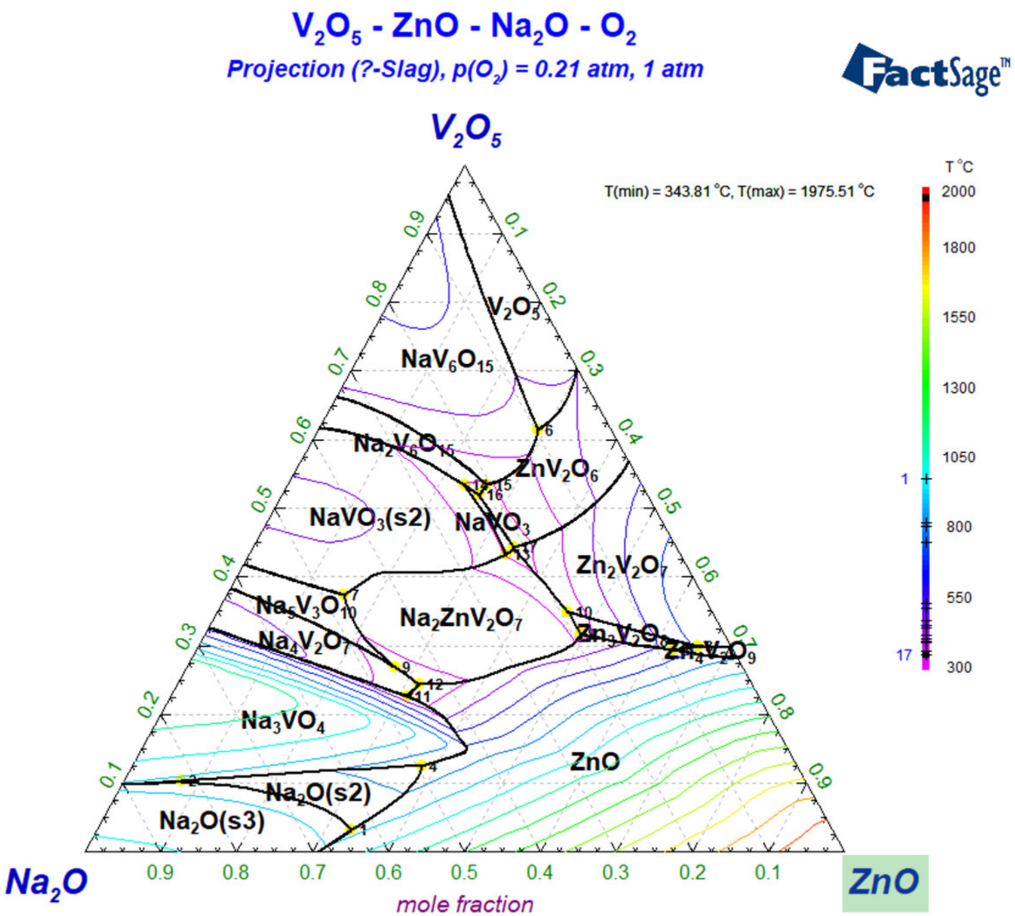


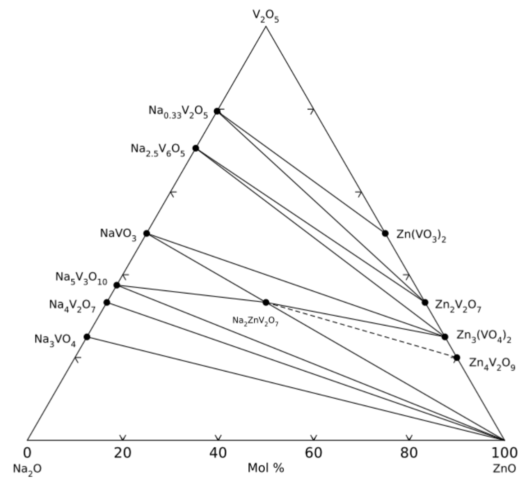


S. F. Blinova, B. V. Slobodin, V. M. Blinov, and A. A. Fotiev, Zh. Neorg. Khim., 31 [8] 2093-2095 (1986);

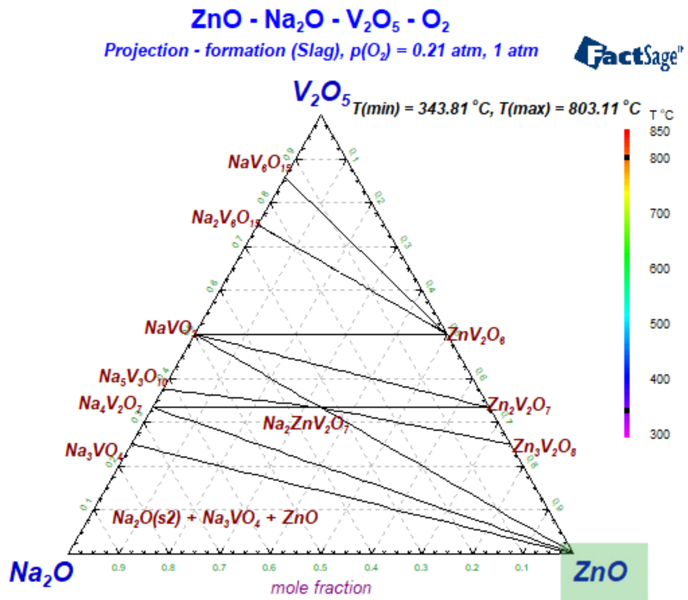
System $ZnO\text{-}Na_2O\text{-}V_2O_5$

$MeO_x\text{-}Na_2O\text{-}V_2O_5$ (Me=Ca, Fe, Zn)





B. V. Slobodin, L. L. Surat, Zh. Neorg. Khim., 51 [9] 1435-1438 (2006)

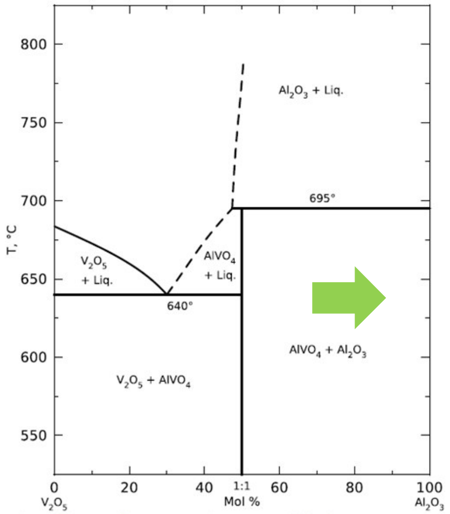


System Al_2O_3-V_2O_5

Database modification

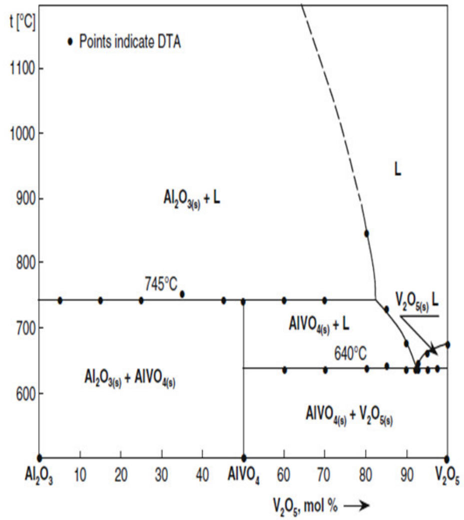
Start:
phase diagram

New literature exp. data:
Phase equilibria + thermodynamic



A. Burdese, Ann. Chim. (Rome), 47 [7-8] 797-805 (1957).

Thermodynamic of $AlVO_4$		
data	**experiment**	**data base**
Cp, LT	Calorimetry [1]	New Cp-function
Cp, HT	DSC [2]	Cp-function from [2]
Cp (298 K), J/mol·K	103.97, drop 103.2 [1,2]	103.9
S_f^0, J/mol·K	91.82 [1]	91.82
ΔH_f^0, kJ/mol	-1578 ± 6 [3], -1651, est. [4]	-1618.29 (new)
$\Delta H_{\text{from oxides}, 298}^0$, kJ/mol	-3.1 ± 2.1 [3]	-4.9
$\Delta H_{\text{from oxides}, 973}^0$, kJ/mol	-40.6 ± 1.5 [3]	-40.8
$H-H_{298}$, kJ/mol	87.67 by DSC [2] 87.44 by drop [2]	87.68



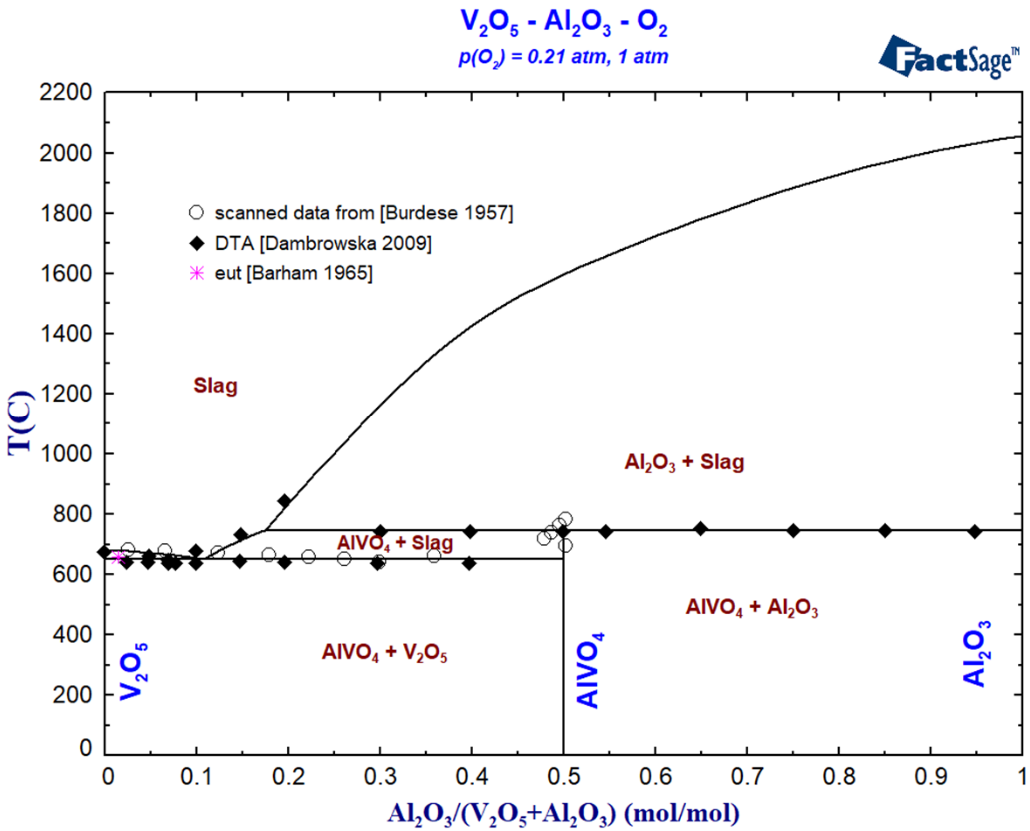
G. Dambrowska, et al., J. Phase Equilib. Diff., 30 [3] 220-229 (2009)

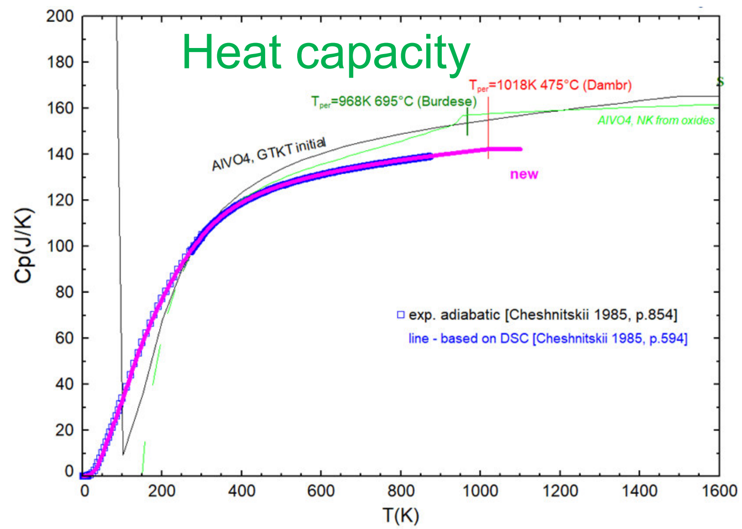
[1] S.M. Cheshnitskii et al., Inorg. Mater. (Engl. Trans.) 21 [6] 854-857 (1985), Izw. Akad. Nauk, Neorg. Mater. 21 [6] 985-988 (1985);
[2] S.M. Cheshnitskii et al., Inorg. Mater. (Engl. Trans.) 21 [4] 594-595 (1985), Izw. Akad. Nauk, Neorg. Mater. 21 [4] 678-679 (1985); Izw. Akad. Nauk, Neorg. Mater. 21 [4] 649-651 (1985);
[4] A.A. Fotiev et al., Russ. J. Inorg. Chem. 28 [1] 119-122 (1983); Trans from Zh. Neorg. Khim. 28 216-219 (1983)

System Al_2O_3-V_2O_5

Re-assessment of the system Al_2O_3-V_2O_5

Results:
Description of $AlVO_4$+phase diagram





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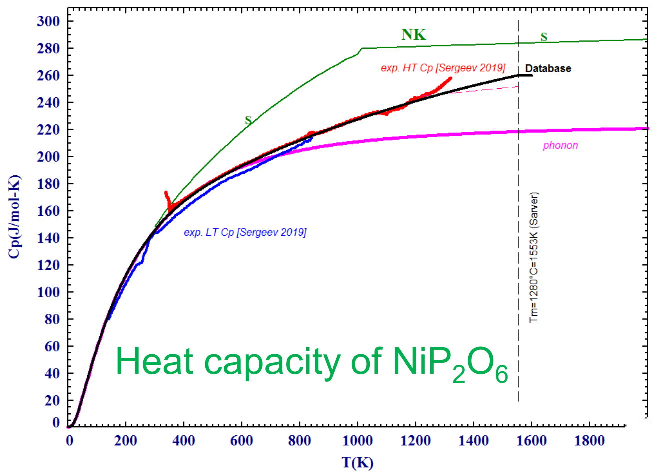
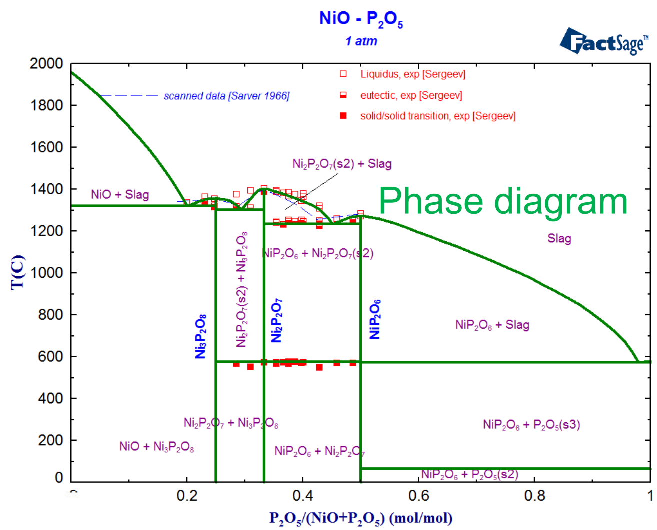
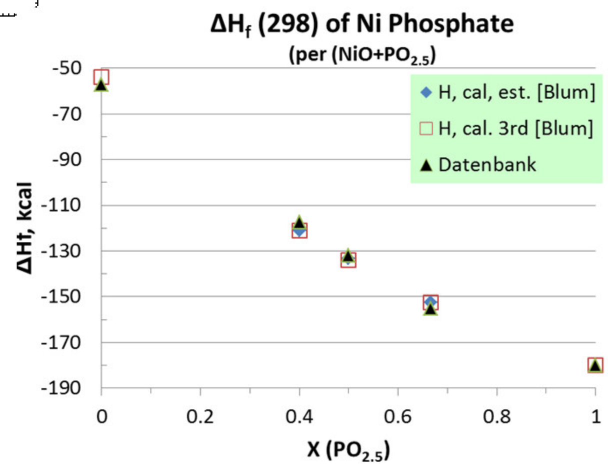
System $NiO-P_2O_5$

Experiment & Modelling

- *Thermal measurements (DTA, DSC) have been performed to obtain thermodynamic properties of $NiPO_x$ (Tm, ΔHm, Ttr, ΔHtr, Cp =f(T)) and phase equilibria $NiO-P_2O_5$*
- *Modelling: new Cp(T) + H, S for $NiPO_x$ have been implemented*

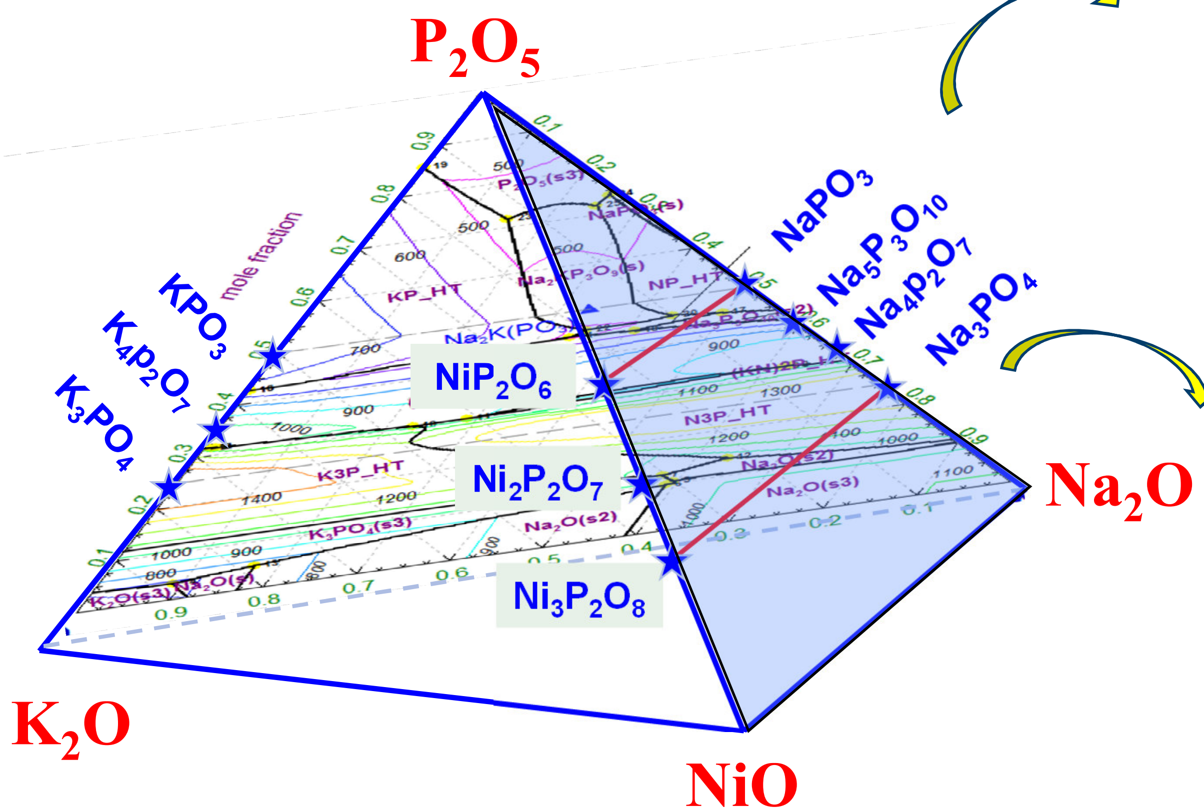


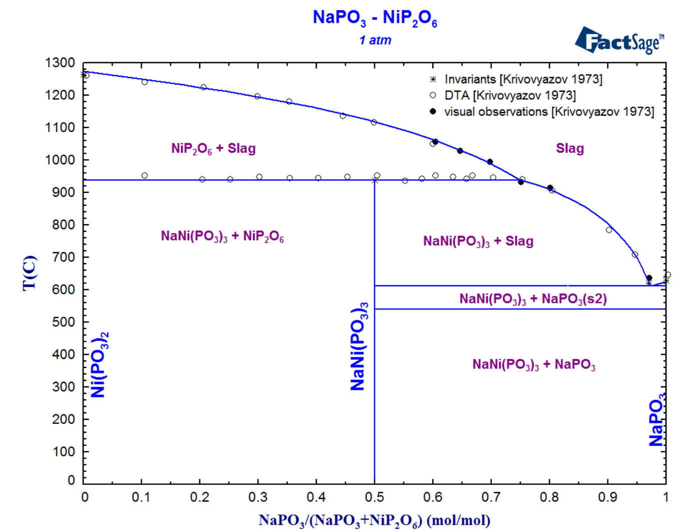


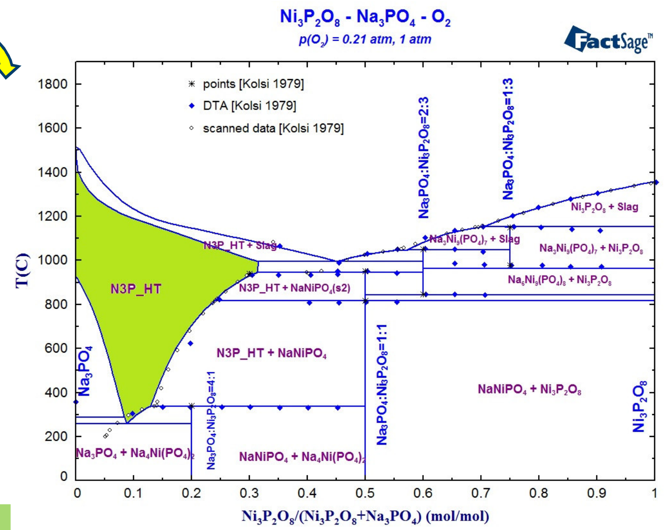


System Alk_2O-NiO-P_2O_5

Database extension (Na_2O)





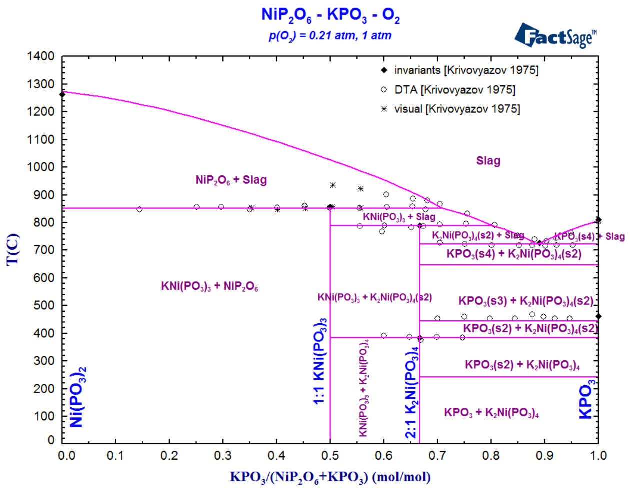


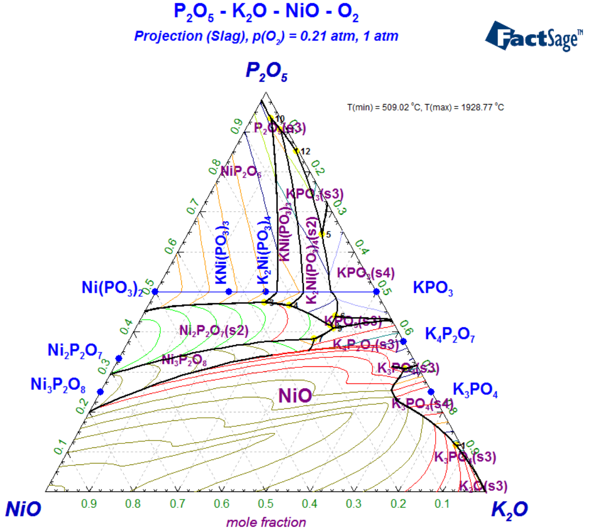
Solubility Na_3PO_4-$Me_3P_2O_8$ (Me=Ca, Mg, **Ni**, Zn)

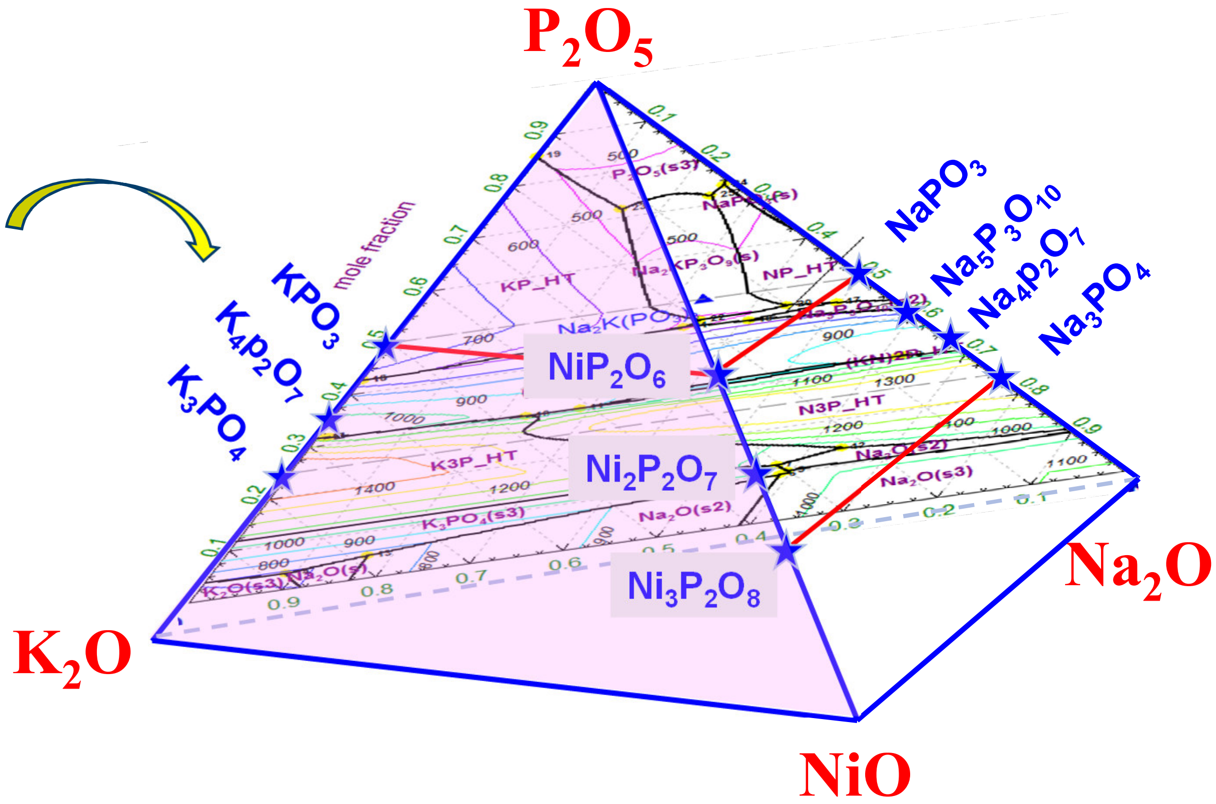
(**Na_2O,** K_2O, ZnO, **NiO**)$_2$(**P_2O_5**)(**Na_2O,** MgO, Na_2MgO_2, Na_2CaO_2)

System Alk_2O-NiO-P_2O_5

Database extending (K_2O)







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Addition of Li_2O

Addition of new oxides (Li_2O, CO_2, SrO, ZrO_2, BaO, La_2O_3, WO_3, H_2O….)

Database development: new component

Quasi-binary systems

- *Li-O*
- *Al_2O_3-Li_2O*
- *CaO-Li_2O*
- *Fe_2O_3-Li_2O*
- *Li_2O-MgO*
- *Li_2O-MnO*
- *Li_2O-Mn_2O_3*
- *Li_2O-Na_2O*
- *Li_2O-NiO*
- *Li_2O-P_2O_5*
- *Li_2O-SiO_2*
- *Li_2O-ZnO*

Ternary systems

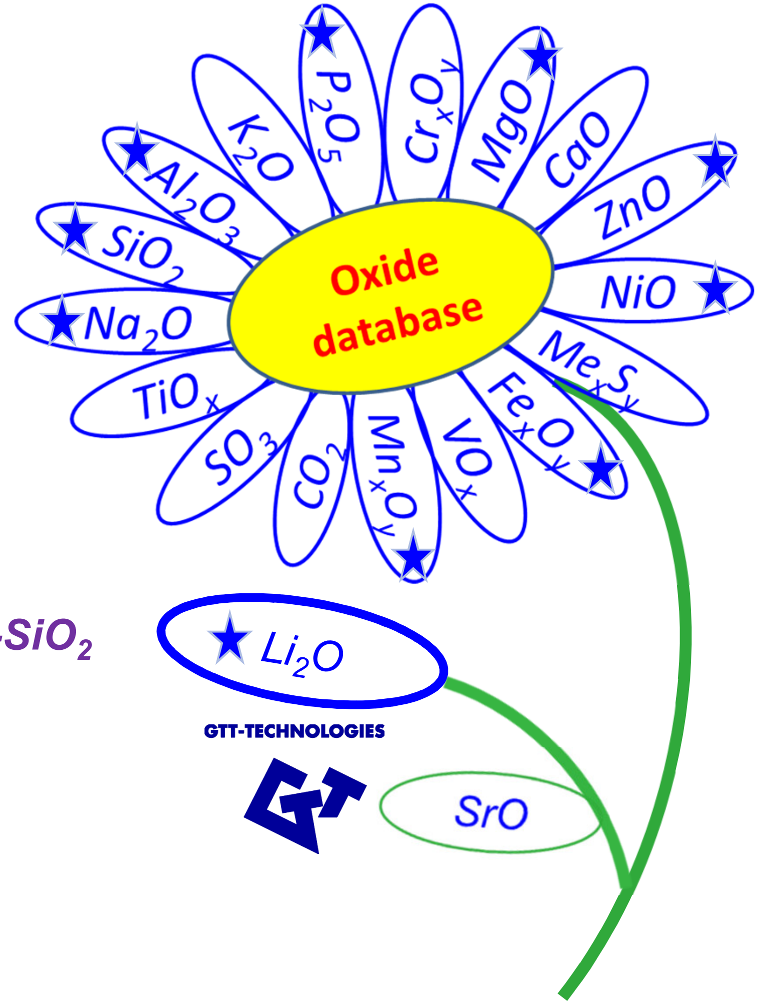
- *Al_2O_3-Fe_2O_3-Li_2O*
- *Al_2O_3-Li_2O-MgO*
- *Al_2O_3-Li_2O-Na_2O*
- *Al_2O_3-Li_2O-SiO_2*
- *CaO-Li_2O-MgO*
- *CaO-Li_2O-SiO_2*
- *Li_2O-MgO-SiO_2*
- *Li_2O-Na_2O-SiO_2*
- *Li_2O-SiO_2-ZnO*

Quaternary system

- *Al_2O_3-Li_2O-Na_2O-SiO_2*

Solutions with Li:

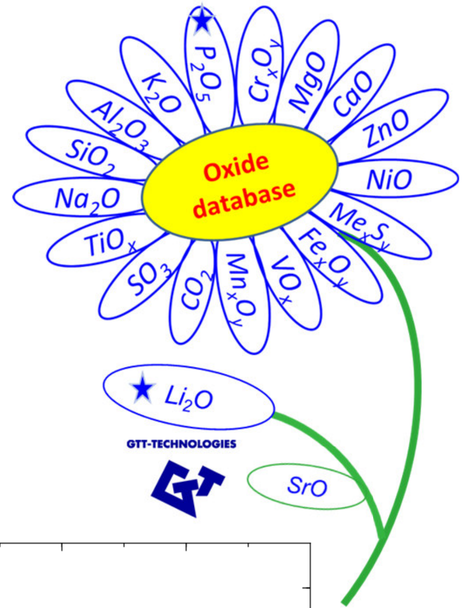
- **Liquid**
- **Slag**
- **Li-Spinel**
- **MeO**
- **Beta-prime**
- **Beta-alumina**

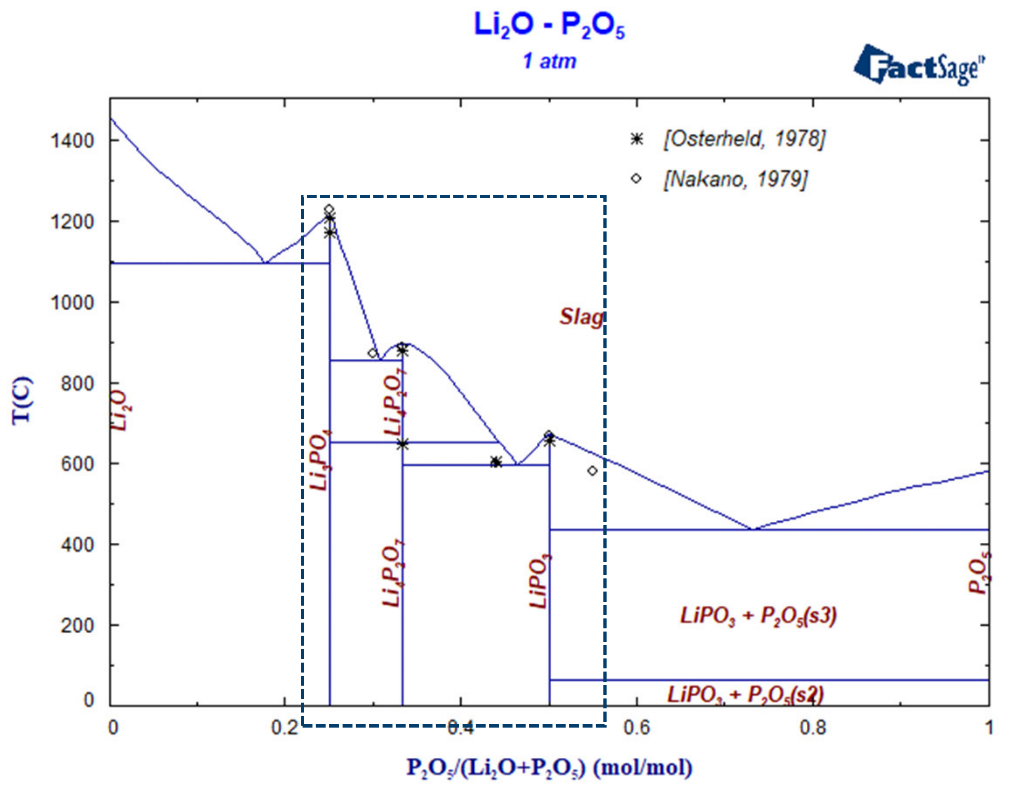


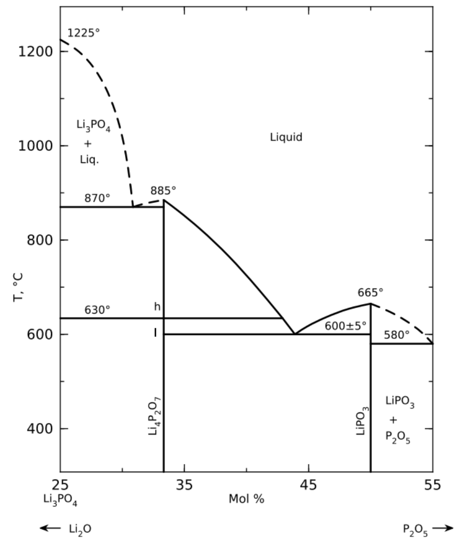
Addition of Li_2O

Phase diagram Li_2O-P_2O_5

✓ *Binary Li phosphates in the slag are similar with those for alkalis (Na, K)*





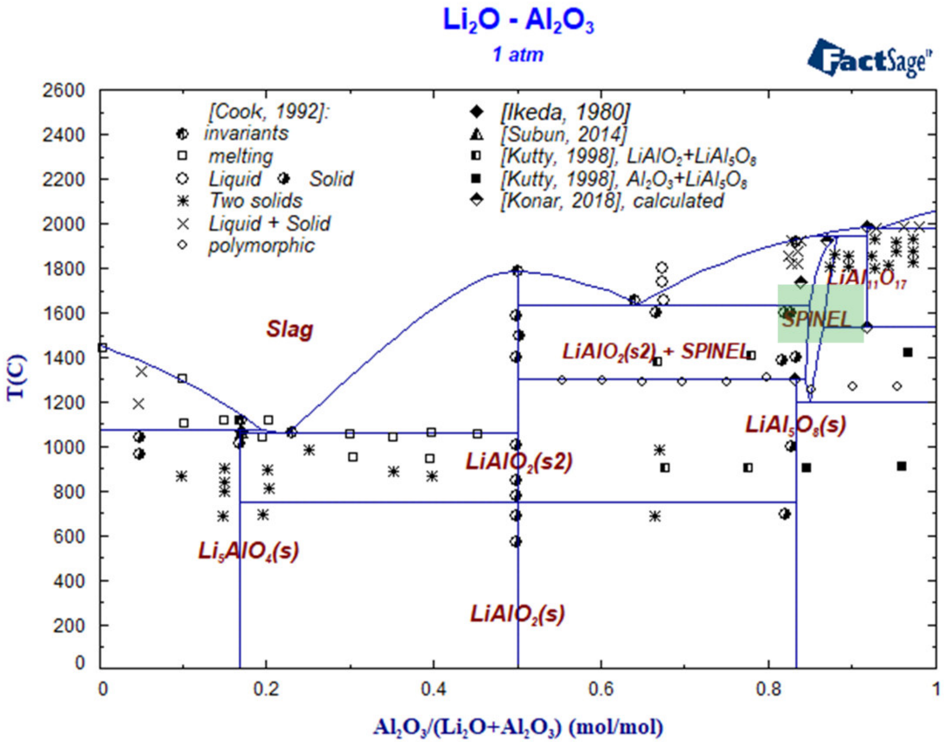


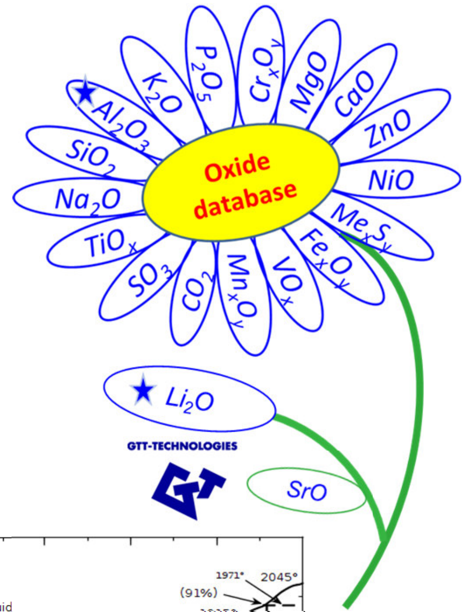
Slag	***(Li_2O, P_2O_5, $LiPO_3$, $Li_4P_2O_7$, Li_3PO_4)***	This work using [Jin, 2019]
$LiPO_3$	***stoichiometric***	[Jin, 2019]
$Li_4P_2O_7$	***stoichiometric***	[Jin, 2019]
Li_3PO_4	***stoichiometric***	[Jin, 2019]

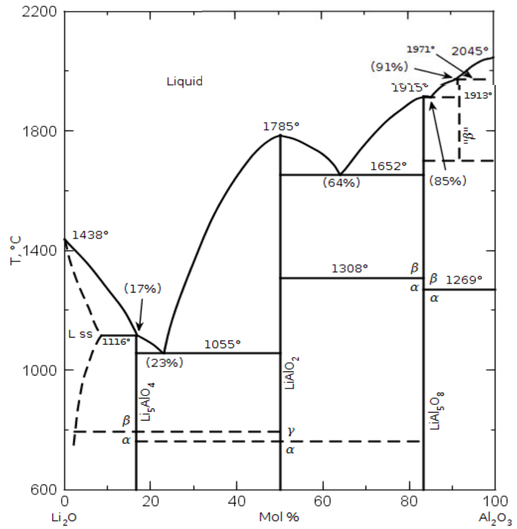
J. Nakano, T. Yamada, S. Miyazawa, J. Am. Ceram. Soc., 62 [9-10] 465-467 (1979)

Addition of Li_2O

Phase diagram Li_2O-Al_2O_3





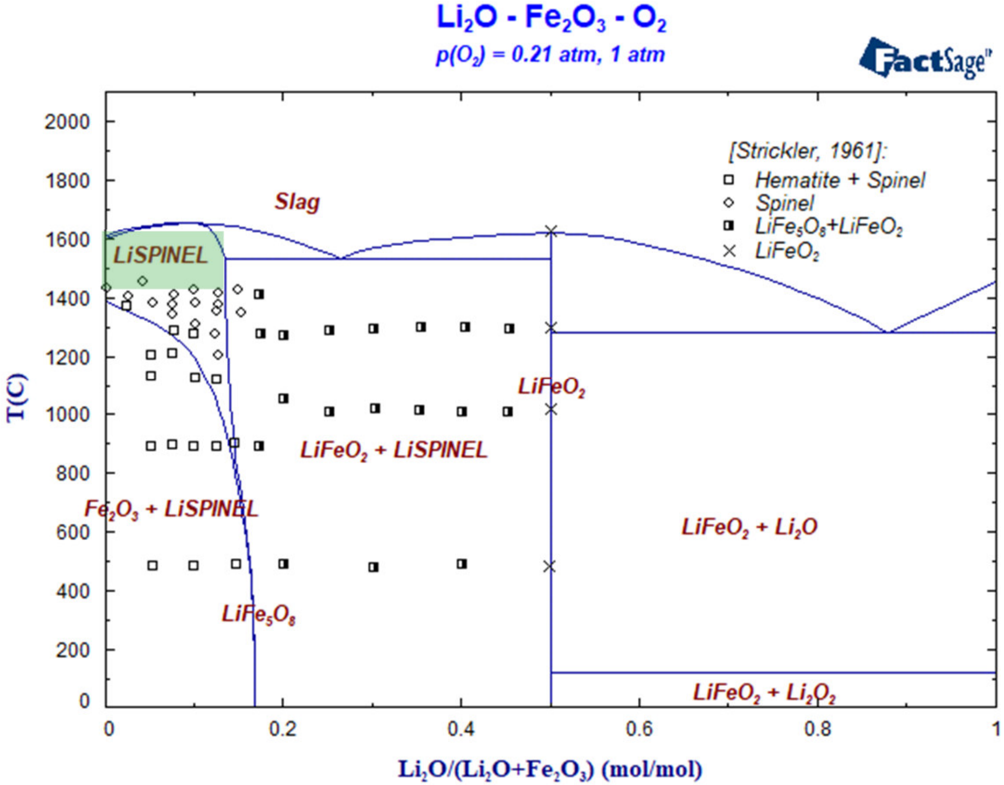


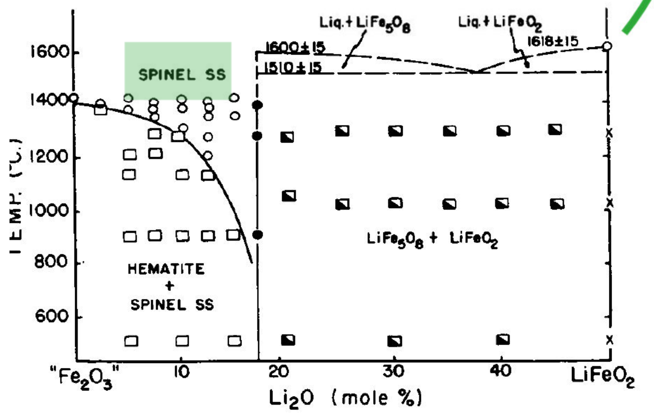
Slag	$(Al_2O_3, Li_2O, LiAlO_2)$	This work
Li-Spinel	$(Al^{+3},Al_{0.5}Li_{0.5}^{+2})(Al^{+3})_2(O^{-2})_4$	This work
$LiAlO_2(s)$	*stoichiometric*	SGPS
$LiAlO_2(s2)$	*stoichiometric*	H_{tr}, T_{tr} [2018Konar]
Li_5AlO_4	*stoichiometric*	This work
$LiAl_5O_8$	*stoichiometric*	This work
$LiAl_{11}O_{17}$	*stoichiometric*	This work
		This work

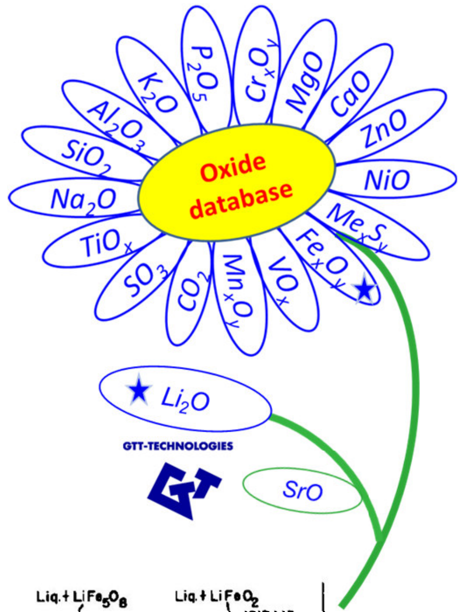
L. P. Cook, E. R. Plante, "Phase Diagram of the System Li2O-Al2O3"; pp. 193-222 in Ceram. Trans., Fabr. Prop. Lithium Ceram. 3, Vol. 27. The American Ceramic Society, Westerville, Ohio, 1992.

Addition of Li_2O

Phase diagram Li_2O-Fe_2O_3





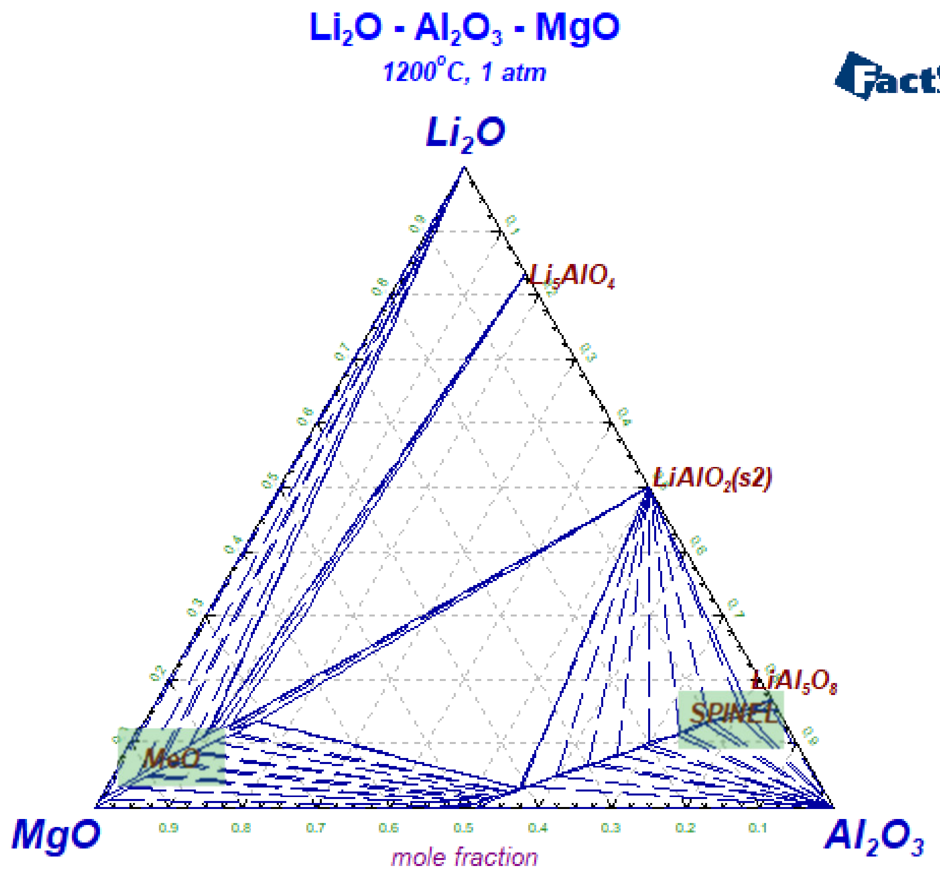


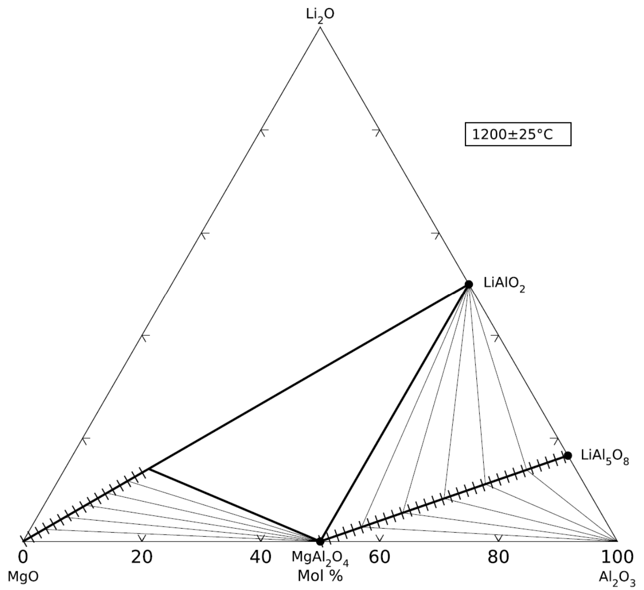
D. W. Strickler, R. Roy, J. Am. Ceram. Soc., 44 [5] 225-230 (1961).

Slag	***(Fe_2O_2, Fe_2O_3, Fe_3O_4, $LiFeO_2$, Li_2O)***	This work
Li-Spinel	***(Fe^{+2},Fe^{+3},$Fe_{0.5}Li_{0.5}{}^{+2}$) (Fe^{+2},Fe^{+3},Va)$_2$(Va)$_2$(O^{-2})$_4$***	This work
$LiFeO_2$	***stoichiometric***	Rakshit 2011
$LiFe_5O_8$	***stoichiometric***	Rakshit 2011

Addition of Li_2O

Isothermal section at 1200°C in Al_2O_3-Li_2O-MgO



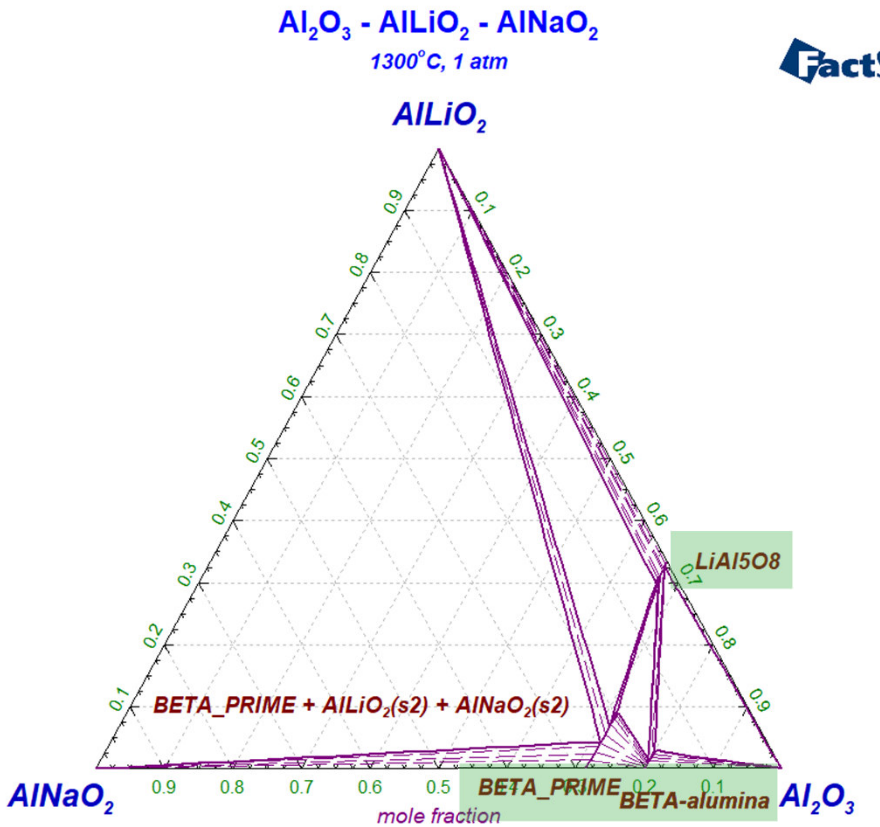


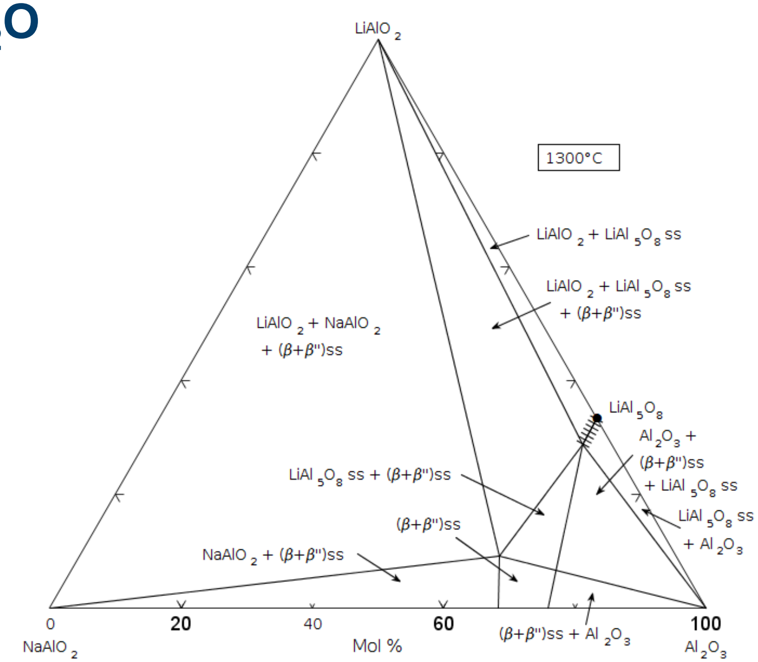
L. T. Menzheres, N. P. Kotsupalo, A. S. Berger, Zh. Neorg. Khim., 23 [10] 2804-2809 (1978).

Slag	***(Al_2O_3, Li_2O, MgO, $AlLiO_2$, Al_2MgO_4)***	**This work**
Li-Spinel	***(Al^{+3}, Mg^{+2},$Al_{0.5}Li_{0.5}{}^{+2}$) (Al^{+3}, Mg^{+2}, Va)$_2$(Mg^{+2}, Va)$_2$(O^{-2})$_4$***	**This work**
MeO	***(Mg^{+2}, $Li_2{}^{+2}$, Va)(O^{-2})***	**This work**

Addition of Li_2O

Isothermal section at 1300°C in Al_2O_3-Li_2O-Na_2O





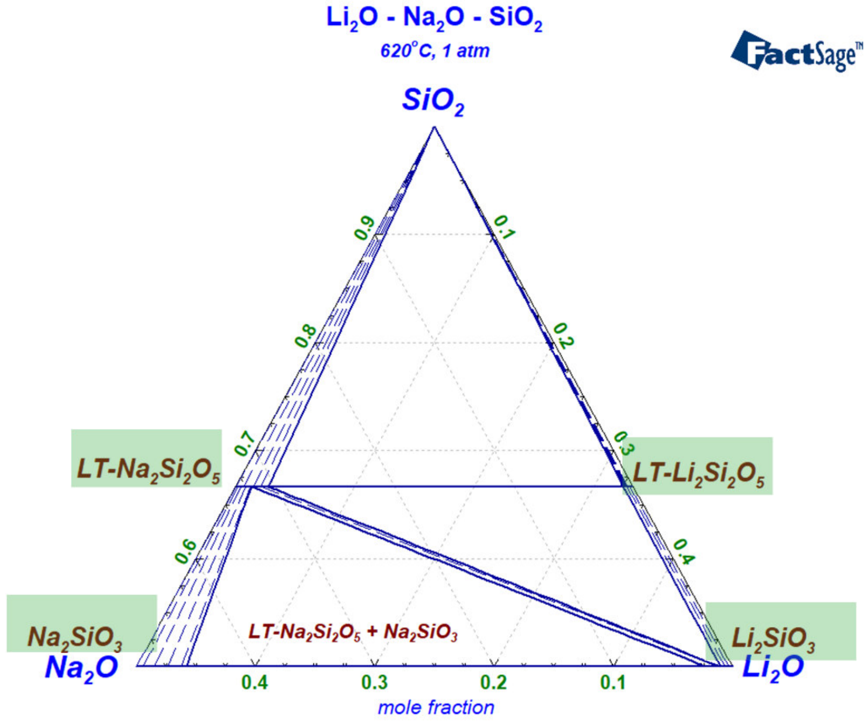
G. K. Duncan and A. R. West, Solid State Ionics, 9-10 [Pt. 1] 259-264 (1983).

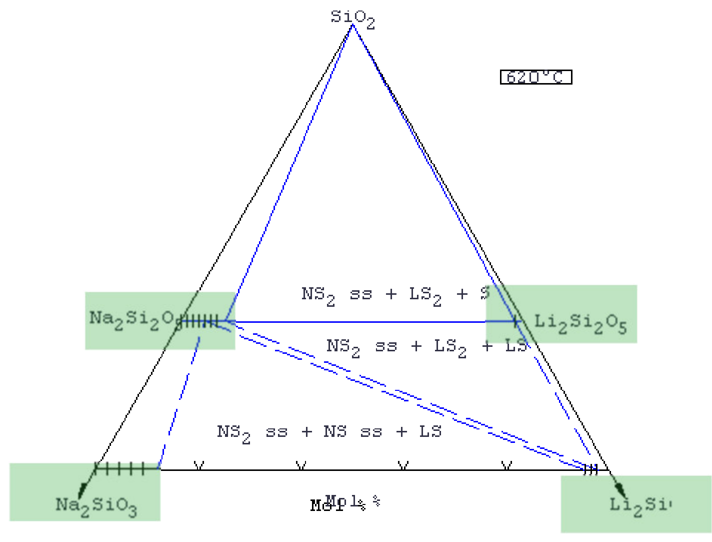
Li-Spinel	$(Al^{+3}, Li_{0.5}Al_{0.5}^{+2}, Na_{0.5}Al_{0.5}^{+2}) (Al^{+3},Va)_2(Va)_2(O^{-2})_4$	This work
Beta-Prime	$(Al)_{12}(\underline{Na}, Li)_2(O)_{19}$	This work
Beta-Alumina	$(Al)_9(\underline{Na}, Li)(O)_{14}$	This work

Addition of Li_2O

GTT-TECHNOLOGIES

Isothermal section at 620°C in Li_2O-Na_2O-SiO_2





A. R. West, J. Am. Ceram. Soc., 59 [3-4], (1976), pp. 124-127.

Slag	$(Li_2O,Na_2O,SiO_2,Li_2SiO_3,Na_2SiO_3,Li_2Si_2O_5,Na_2SiO_5,Li_4SiO_4,Na_4SiO_4)$	This work
$HT\text{-}Na_2Si_2O_5$, $MT\text{-}Na_2Si_2O_5$, $LT\text{-}Na_2Si_2O_5$	$(\underline{Na^{+1}}, Li^{+1})_2(Si^{+4})_2(O^{-2})_5$	This work
$HT\text{-}Li_2Si_2O_5$, $LT\text{-}Li_2Si_2O_5$	$(\underline{Li^{+1}}, Na^{+1})_2(Si^{+4})_2(O^{-2})_5$	This work
Na_2SiO_3	$(\underline{Na^{+1}}, Li^{+1})_2(Si^{+4})(O^{-2})_3$	This work
Li_2SiO_3	$(\underline{Li^{+1}}, Na^{+1})_2(Si^{+4})(O^{-2})_3$	This work

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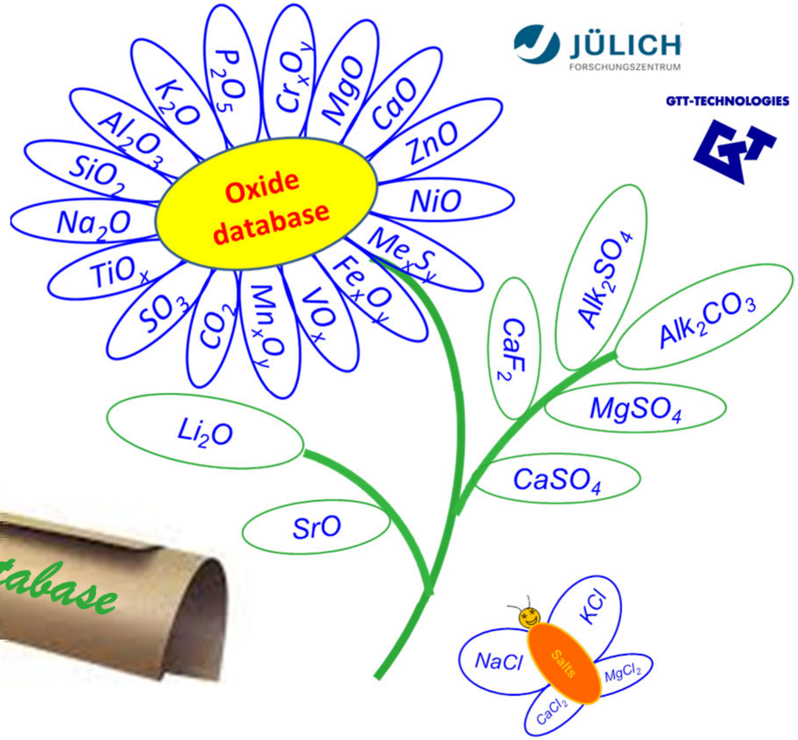
Conclusions



HOTVEGAS
Hochtemperaturvergasung und Gasreinigung

Basic experiments and thermochemical modelling

Experiments

(slag, membranes, trace elements, etc.; with TA, XRD, KEMS, MBMS, Visco, etc.)

Database development

Work on various sub-systems for the purpose of database` completeness (SO_3, TiO_2, V_2O_5, NiO, P_2O_5)

Addition of new oxides (Li_2O, CO_2, SrO, ZrO_2, BaO, La_2O_3, WO_3, H_2O….)

Oxide database	Atlas (16.0) June 2020
Binary systems	213
Ternary systems	177
Quaternaries	9
Slag components	244
Solid solution phases	157
Stoichiometric compounds	880

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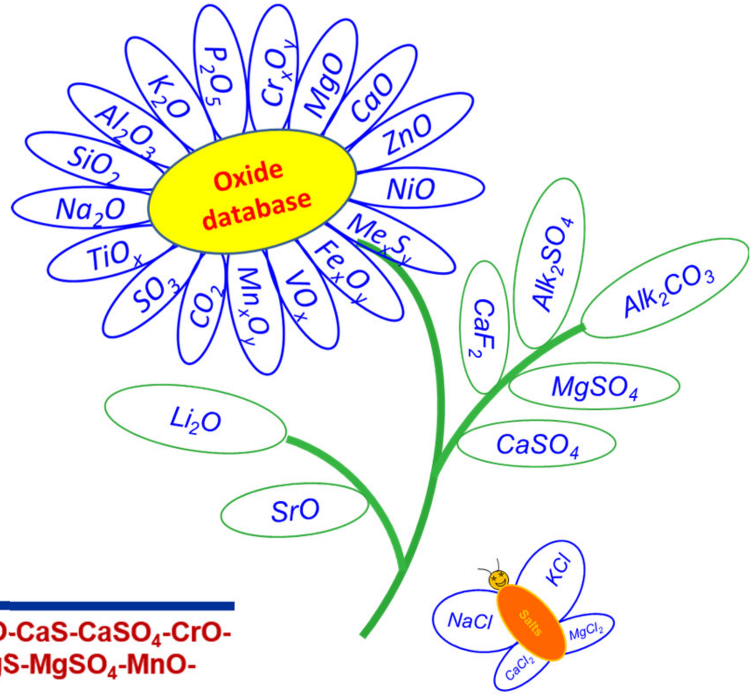
On behalf of all co-authors:

Thank you for your attention!

Vielen Dank für Ihre Aufmerksamkeit!

Благодарю за внимание!

e.yazhenskikh@fz-juelich.de



Present state of GTOX database

GTT-Technologies

The GTOX database contains the assessment of the Al_2O_3-Al_2S_3-CaF_2-CaO-CaS-$CaSO_4$-CrO-Cr_2O_3-CrS-FeO-Fe_2O_3-FeS-K_2O-K_2S-K_2SO_4-Na_2O-Na_2S-Na_2SO_4-Li_2O-MgO-MgS-$MgSO_4$-MnO-Mn_2O_3-MnS-NiO-NiS-P_2O_5-SiO_2-SrO-TiO_2-Ti_2O_3-V_2O_3-V_2O_5-ZnO system

Contents	*Slagatlas, Year*									
	2.0 2010	3.0 2011	9.0 2014	10.0 2015	11.0 2015	12.0 2017	13 2017	14 2018	15 2019	16 2020
Binary systems	24	26	89	109	116	130	134	171	188	213
Ternary systems	11	34	75	80	97	110	124	141	149	177
Quaternaries	-	5	6	6	6	7	7	7	8	9
Slag components	48	50	113	132	151	166	173	199	209	244
Liquid components	9	9	19	25	27	28	29	30	34	44
Solid solution phases	32	41	68	75	85	102	104	112	123	157
Stoichiometric phases	112	145	291	339	422	482	490	596	647	880
Total pages	157	281	648	706	850	920	1001	1142	1245	≈1400