Addition of ZnO to the HotVeGas Oxide database

GTT-Technologies

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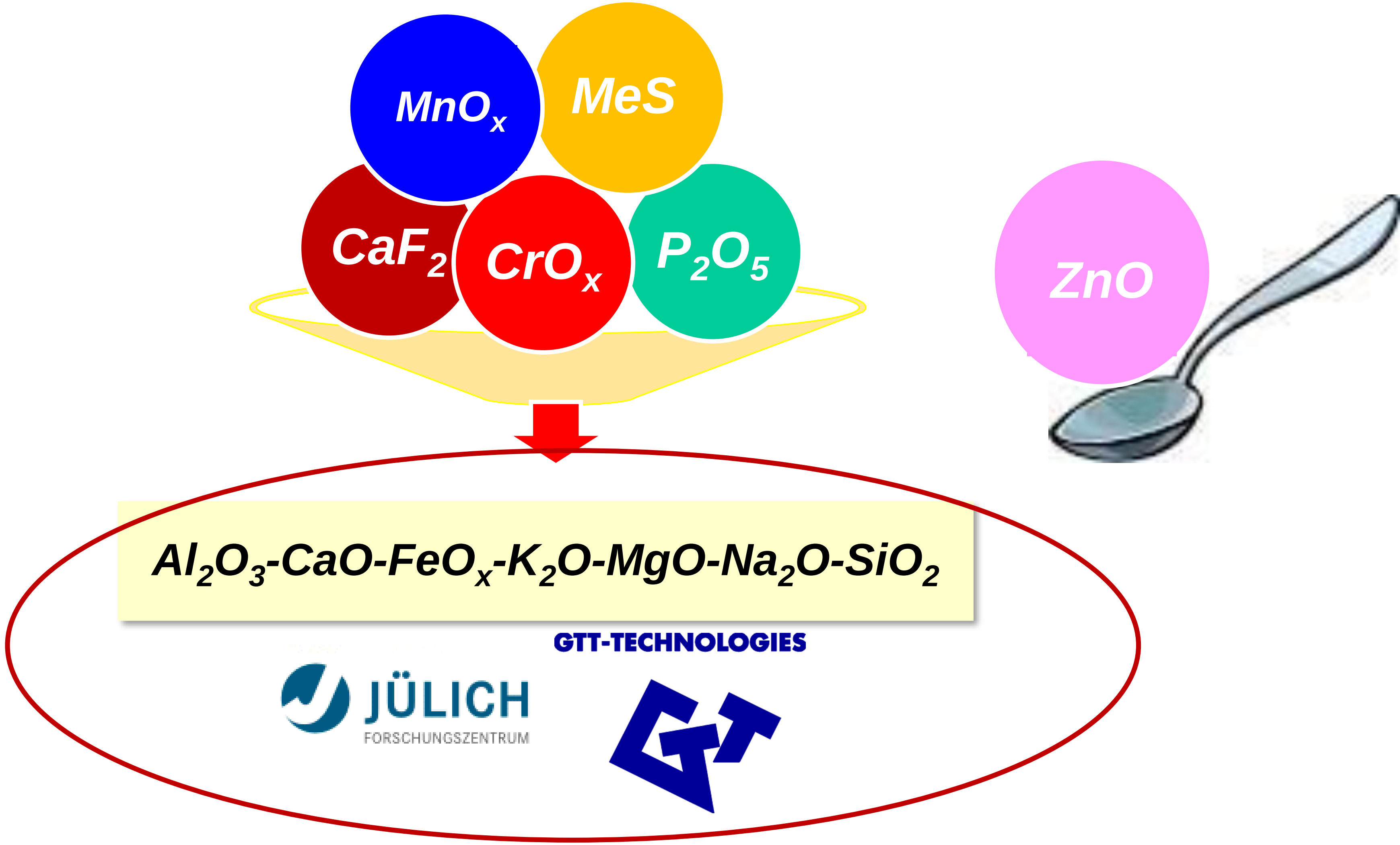
Contents of presentation

- Introduction
- Solid solution phases
- Ternary systems
- Conclusions
- Future developments

HotVeGas Oxide database



Addition of ZnO

- The Al_2O_3-ZnO system
- The CaO-ZnO system
- The CrO_x-ZnO system
- The FeO_x-ZnO system
- The MgO-ZnO system
- The MnO_x-ZnO system
- The P_2O_5-ZnO system
- The SiO_2-ZnO system
    - The ternary CaO-SiO_2-ZnO system
    - The ternary FeO_x-SiO_2-ZnO system
    - The ternary MgO-SiO_2-ZnO system
    - The ternary MnO-SiO_2-ZnO system
    - The ternary Na_2O-SiO_2-ZnO system

Addition of ZnO

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The associate species containing Zn were added in order to describe the liquid phase in the Al_2O_3-CaO-CrO_x-FeO_x-K_2O-MgO-MnO_x-Na_2O-P_2O_5-SiO_2 system containing ZnO.

System	Associate species	Description MeO_x : ZnO
Al_2O_3- ZnO	Al_2ZnO_4	1:1
Cr_2O_3 – ZnO	Cr_2ZnO_4	
Fe_2O_3 – ZnO	Fe_2ZnO_4	
Mn_2O_3 – ZnO	Mn_2ZnO_4	
P_2O_5-ZnO	ZnP_2O_6, $Zn_2P_2O_7$, $Zn_3P_2O_8$ (like with Ca^{+2}, Fe^{+2}, Mg^{+2}, Mn^{+2})	1:1, 2:1, 3:1
SiO_2-ZnO	Zn_2SiO_4	1:2

Modelling of binary Zn-containing phases

System	*Phase*	*Description*	*Source*
Al_2O_3-ZnO	Cubic spinel	$(Al^{+3},\underline{Zn}^{+2})(Al^{+3})_2\ (O^{-2})_4$	Al_2ZnO_4(SGPS)
CaO-ZnO	MeO	$(Ca^{+2},Zn^{+2},Va)(O^{-2})$	This work
CrO_x-ZnO	Zincite Cubic spinel	$(\underline{Zn}^{+2}, Cr^{+3}, Va)(O^{-2})$ $(\underline{Cr}^{+2},Cr^{+3}, \underline{Zn}^{+2})(\underline{Cr}^{+3},Va)_2\ (\underline{Va},Cr^{+2})_2(O^{-2})_4$	This work Cr_2ZnO_4(SGPS)
FeO_x-ZnO	Zincite MeO Cubic spinel	$(\underline{Zn}^{+2}, Fe^{+2}, Fe^{+3}, Va)(O^{-2})$ $(\underline{Fe}^{+2},Fe^{+3},Zn^{+2}, Va)(O^{-2})$ $(\underline{Fe}^{+2},Fe^{+3},\underline{Zn}^{+2})(Fe^{+2},\underline{Fe}^{+3},Va)_2(Va,Fe^{+2})_2(O^{-2})_4$	This work This work Fe_2ZnO_4(SGPS)
MgO-ZnO	MeO Zincite	$(\underline{Mg}^{+2},Zn^{+2},Va)(O^{-2})$ $(\underline{Zn}^{+2}, Mg^{+2}, Va)(O^{-2})$	This work This work

Modelling of binary Zn-containing phases

System	Phase	Description	Source
MnO_x-ZnO	MeO Zincite Cubic spinel Tetragonal spinel	*(<u>Mn</u>$^{+2}$, Mn^{+3},Zn^{+2},Va)(O^{-2})* *(<u>Zn</u>$^{+2}$, Mn^{+2}, Mn^{+3},Va)(O^{-2})* *(<u>Mn</u>$^{+2}$,<u>Zn</u>$^{+2}$)(Mn^{+2},<u>Mn</u>$^{+3}$,Mn^{+4},Va)$_2$(Va)$_2$(O^{-2})$_4$* *(<u>Mn</u>$^{+2}$,Mn^{+3},Zn^{+2})(Mn^{+2},<u>Mn</u>$^{+3}$,Va)$_2$(O^{-2})$_4$*	This work This work Mn_2ZnO_4, H_f and S_f [99Youn]
P_2O_5-ZnO	ZnP_4O_{11} ZnP_2O_6 $Zn_2P_2O_7$ $Zn_3P_2O_8$	Stoichiometric Stoichiometric Stoichiometric Stoichiometric	This work This work This work SGPS changed
SiO_2-ZnO	Zn_2SiO_4	Stoichiometric	SGPS

Modelling of ternary Zn-containing phases

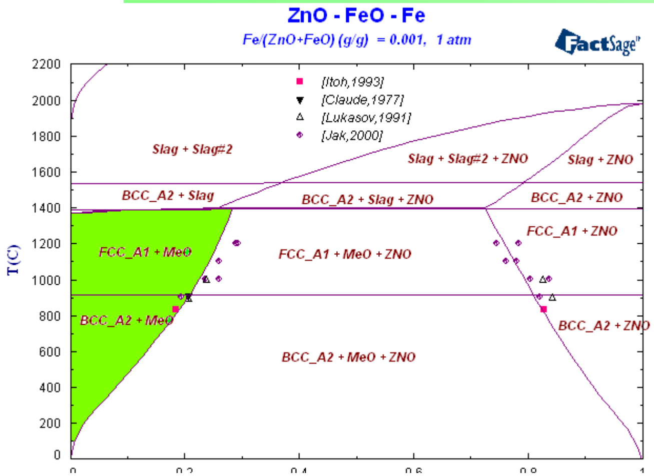
System	Phase	Description	Source
$CaO-SiO_2-ZnO$	$Ca_2ZnSi_2O_7$	Stoichiometric	FTOxide changed
	$\alpha'-Ca_2SiO_4$	$(\underline{Ca}^{+2},Zn^{+2})(Ca^{+2},\underline{Va})_2(Si^{+4})_2(O^{-2})_4$	This work
	Olivine	$(\underline{Ca}^{+2}, Zn^{+2})(Ca^{+2})(Si^{+4})(O^{-2})_4$	This work
$FeO-SiO_2-ZnO$	Olivine	$(\underline{Fe}^{+2}, Zn^{+2})(Fe^{+2})(Si^{+4})(O^{-2})_4$	This work
	Willemite	$(\underline{Zn}^{+2},Fe^{+2})(Si^{+4})_2(O^{-2})_4$	This work
$MgO-SiO_2-ZnO$	Olivine	$(\underline{Mg}^{+2}, Zn^{+2})(Mg^{+2})(Si^{+4})(O^{-2})_4$	This work
	Willemite	$(\underline{Zn}^{+2},Mg^{+2})(Si^{+4})_2(O^{-2})_4$	This work
	Protopyroxene	$(\underline{Mg}^{+2},Zn^{+2})(Si^{+4})(O^{-2})_3$	This work
$MnO-SiO_2-ZnO$	Olivine	$(\underline{Mn}^{+2}, Zn^{+2})(Mn^{+2})(Si^{+4})(O^{-2})_4$	This work
Na_2O-SiO_2-ZnO	NZS	Na_2ZnSiO_4	This work
	NZS2	$Na_2ZnSi_2O_6$	This work
	NZ2S2	$Na_2Zn_2Si_2O_7$	This work
	N2Z2S3	$Na_4Zn_2Si_3O_{10}$	This work

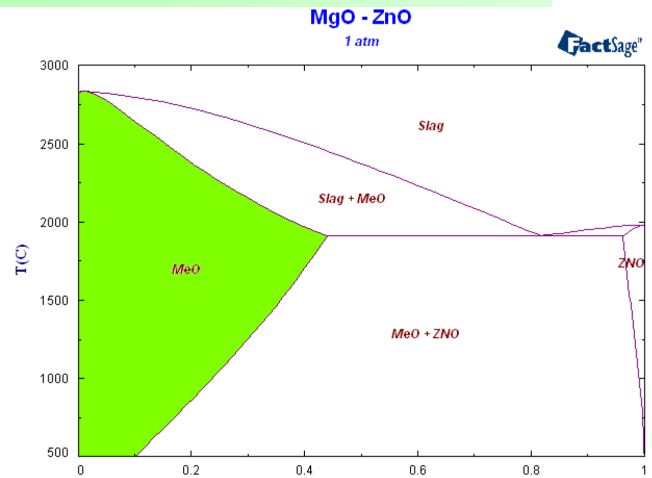
Modelling of Zn-containing phases

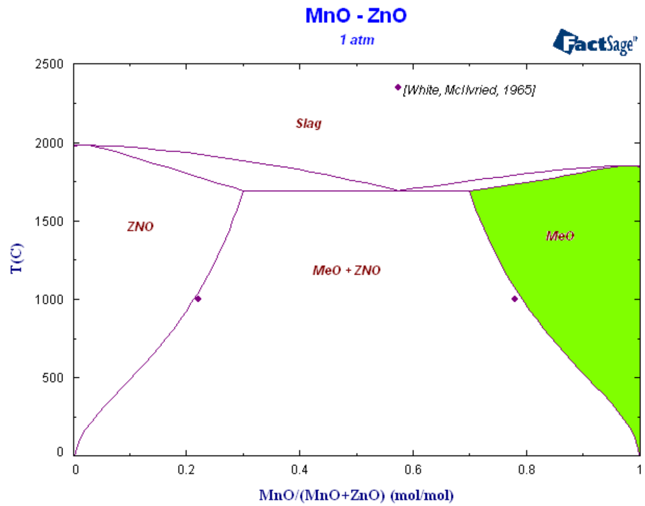
Phase	Description
MeO	$(Al^{+3},Ca^{+2},Cr^{+3},Mn^{+2},Mn^{+3},Fe^{+2},Fe^{+3},Mg^{+2},Na^{+1}, Zn^{+2},Va)(O^{-2})$
Cubic Spinel	$(Al^{+3},Cr^{+2},Cr^{+3},Fe^{+2},Fe^{+3},Mg^{+2},Mn^{+2},Zn^{+2})(Al^{+3},Ca^{+2},Cr^{+3},Fe^{+2},Fe^{+3},Mg^{+2},Mn^{+2},Mn^{+3},Mn^{+4},Va)_2\ (Cr^{+2}, Fe^{+2}, Mg^{+2},Va)_2(O^{-2})_4$
Tetragonal Spinel	$(Cr^{+2}, Cr^{+3},Mn^{+2},Mn^{+3},Zn^{+2})(Al^{+3},Cr^{+3},Fe^{+3},Mn^{+2},Mn^{+3},Va)_2(O^{-2})_4$
Zincite	$(Ca^{+2},Cr^{+3},Mn^{+2},Mn^{+3},Fe^{+2},Fe^{+3},Mg^{+2},\underline{Zn}^{+2},Va)(O^{-2})$
Willemite	$(\underline{Zn}^{+2},Mg^{+2},Fe^{+2})(Si^{+4})_2(O^{-2})_4$
Olivine	$(Ca^{+2}, Fe^{+2},Mg^{+2},Mn^{+2},Zn^{+2})(Ca^{+2},Fe^{+2},Mg^{+2},Mn^{+2})(Si^{+4})(O^{-2})_4$
α'-Ca_2SiO_4	$(\underline{Ca}^{+2},Fe^{+2},Mg^{+2}, Mn^{+2},Zn^{+2})(Ca^{+2},\underline{Va})_2(P^{+5},\underline{Si}^{+4})_2(O^{-2})_4$
Protopyroxene	$(Ca^{+2},Mg^{+2},Mn^{+2},Zn^{+2})(Si^{+4})(O^{-2})_3$

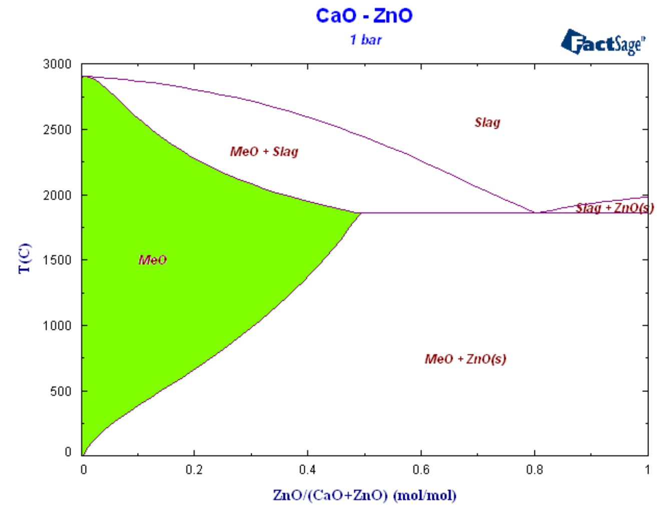
Description of the phase MeO

MeO - $(Al^{+3},\underline{Ca}^{+2},Cr^{+3},\underline{Mn}^{+2},Mn^{+3},\underline{Fe}^{+2},Fe^{+3},\underline{Mg}^{+2},Na^{+1}, Zn^{+2},Va)(O^{-2})$









Description of the phase Zincite

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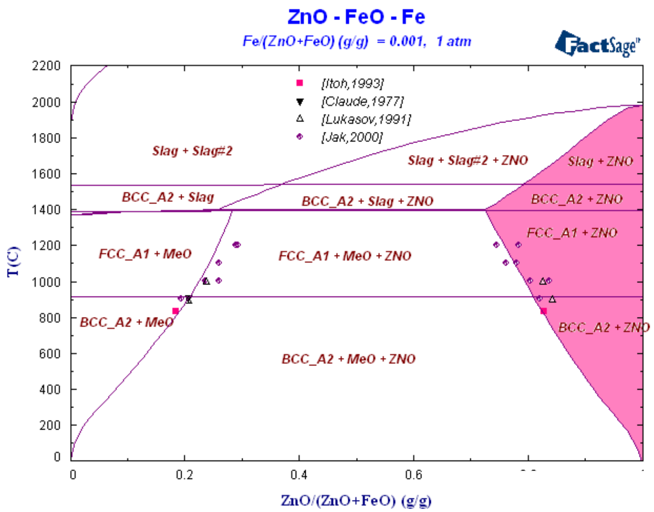
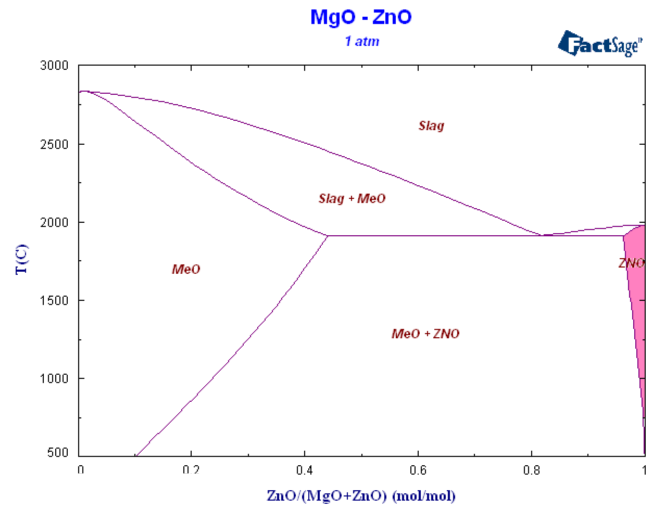
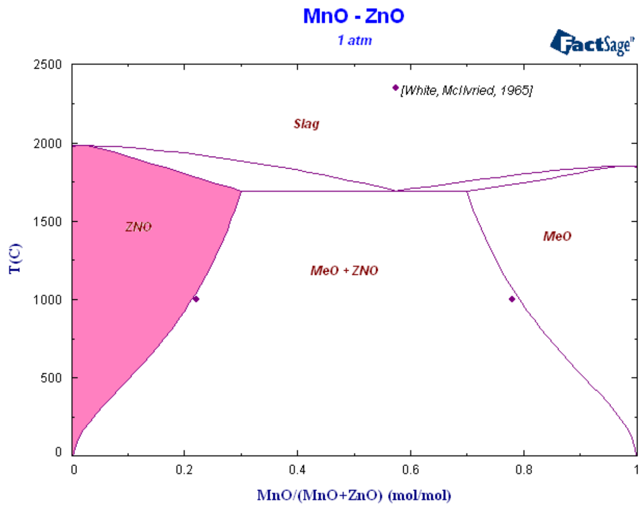
Zincite - $(Ca^{+2},Cr^{+3},Mn^{+2},Mn^{+3},Fe^{+2},Fe^{+3},Mg^{+2},\underline{Zn}^{+2},Va)(O^{-2})$

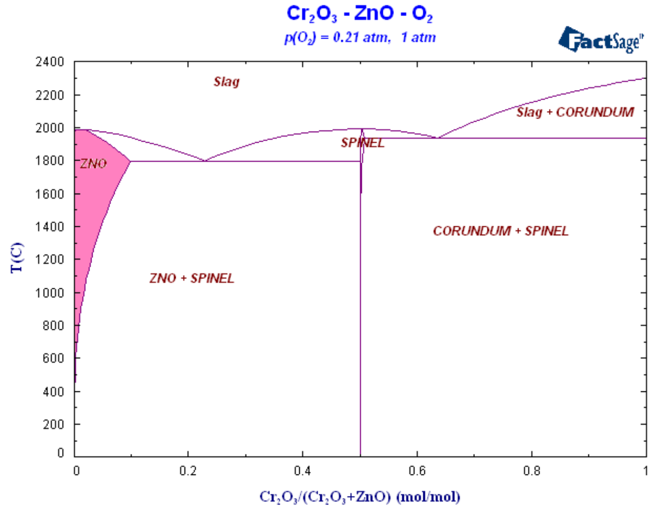


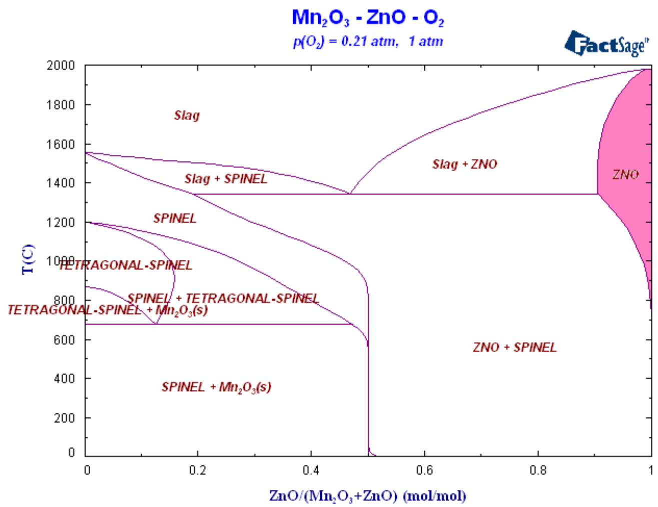


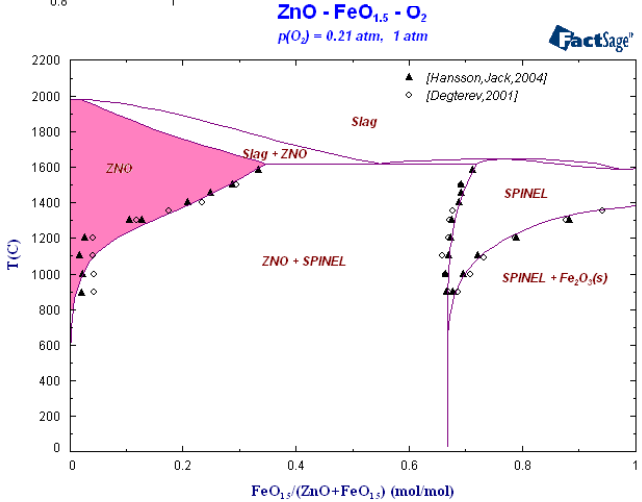


Description of the phase Zincite

Zincite - $(Ca^{+2},Cr^{+3},Mn^{+2},Mn^{+3},Fe^{+2},Fe^{+3},Mg^{+2},\underline{Zn}^{+2},Va)(O^{-2})$







Modelling of Spinel

Zn^{+2}

Spinel $(Al^{+3},Cr^{+2},Cr^{+3},Fe^{+2},Fe^{+3},Mg^{+2},Mn^{+2})(Al^{+3},Ca^{+2},Cr^{+3},Fe^{+2},Fe^{+3},Mg^{+2},Mn^{+2},Mn^{+3},Mn^{+4},Va)_2\ (Cr^{+2},Fe^{+2},Mg^{+2},Va)_2(O^{-2})_4$ *280 Gibbs energies*

=

+ 40 Gibbs energies of real Spinels (SGPS) and fictive compounds = 320 Gibbs energies

The following reciprocal equations were applied:

$G(Me_2:Me_1:Va:O) + G(Me_1:Va:Va:O) = G(Me_1:Me_1:Va:O) + G(Me_2:Va:Va:O)$

Some simplifications were applied:

$*:*:Fe^{+2}:O^{-2} = *:*:Va:O^{-2} + 2G + D - B$ *[91Sundman]*

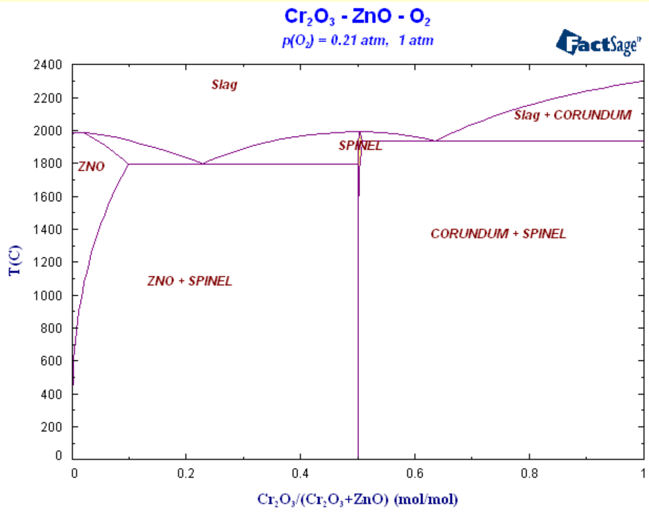
$*:*:Cr^{+2}:O^{-2} = *:*:Fe^{+2}:O^{-2}$ *[08Kjellqvist]*

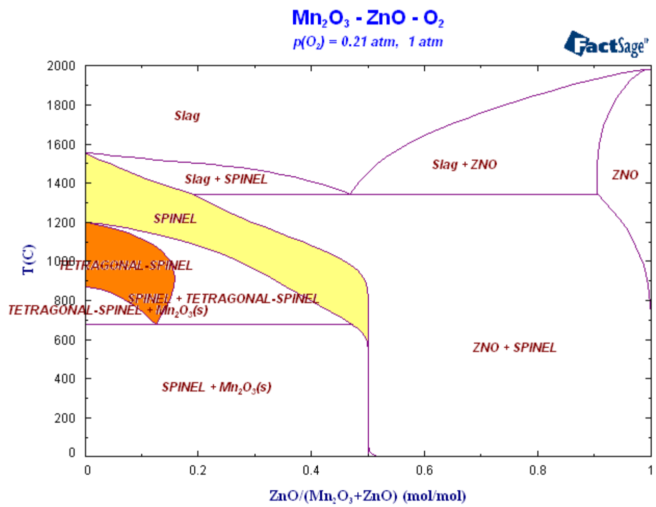
$*:*:Mg^{+2}:O^{-2} = *:*:Va:O^{-2} + K$ *This work*

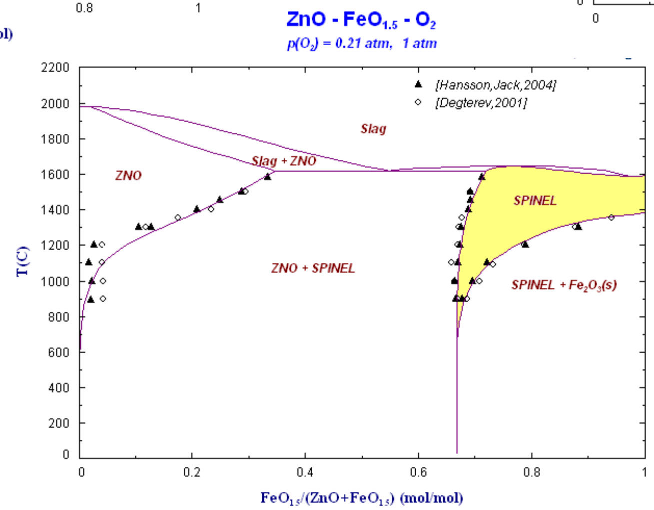
$G(Zn^{+2}:Me^{+2}:Va:O) = 0.33*G(Zn^{+2}:Va:Va:O) + 0.66*G(Me^{+2}:Me^{+2}:Va:O)$

Description of the phase Spinel

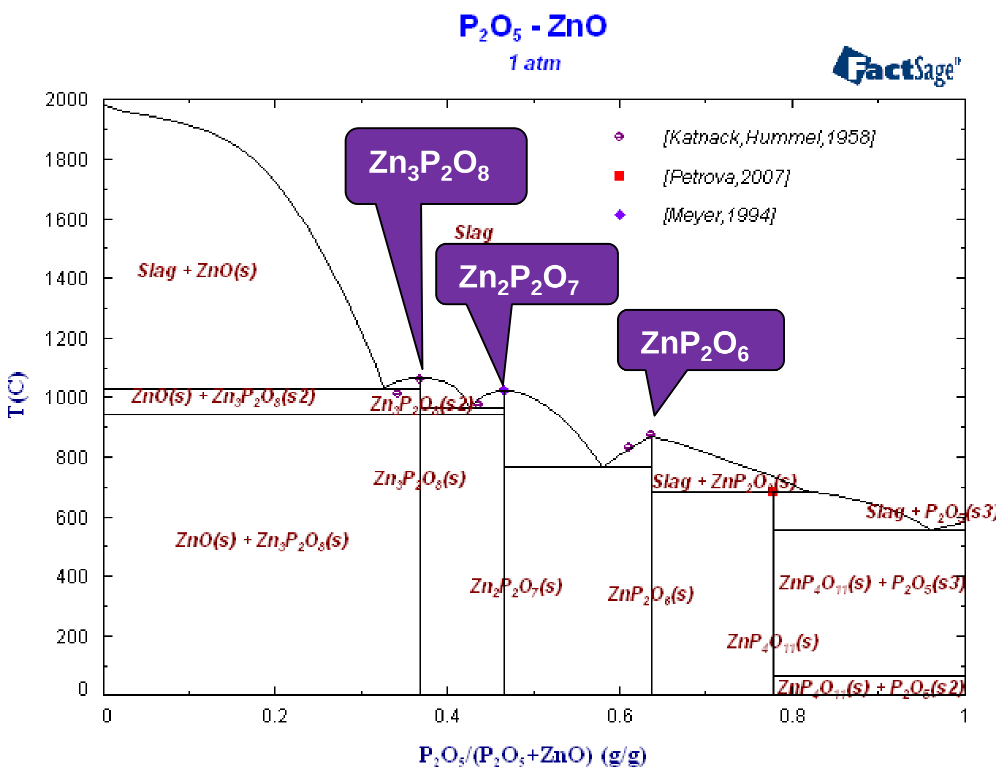
Spinel $(Al^{+3},Cr^{+2},Cr^{+3},Fe^{+2},Fe^{+3},Mg^{+2},Mn^{+2},Zn^{+2})(Al^{+3},Ca^{+2},Cr^{+3},Fe^{+2},Fe^{+3},Mg^{+2},Mn^{+2},Mn^{+3},Mn^{+4},Va)_2\ (Cr^{+2}, Fe^{+2}, Mg^{+2},Va)_2(O^{-2})_4$

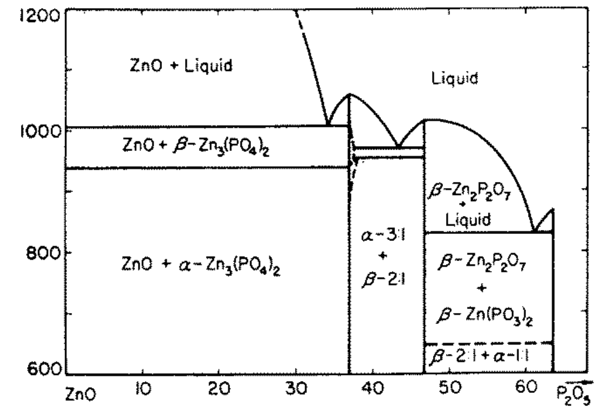




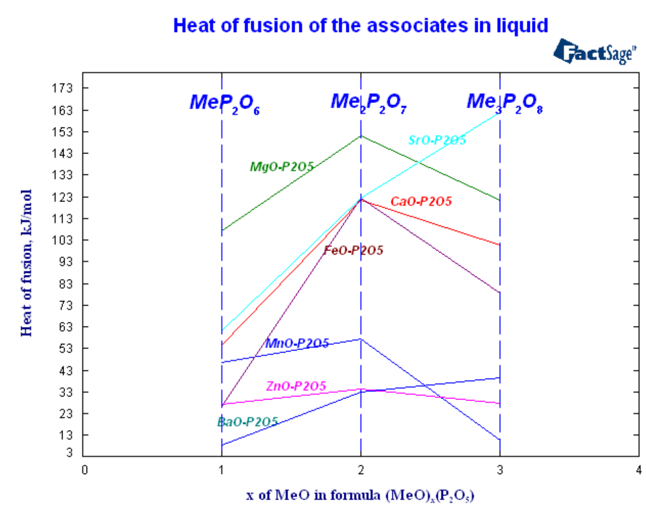


P_2O_5–ZnO phase diagram

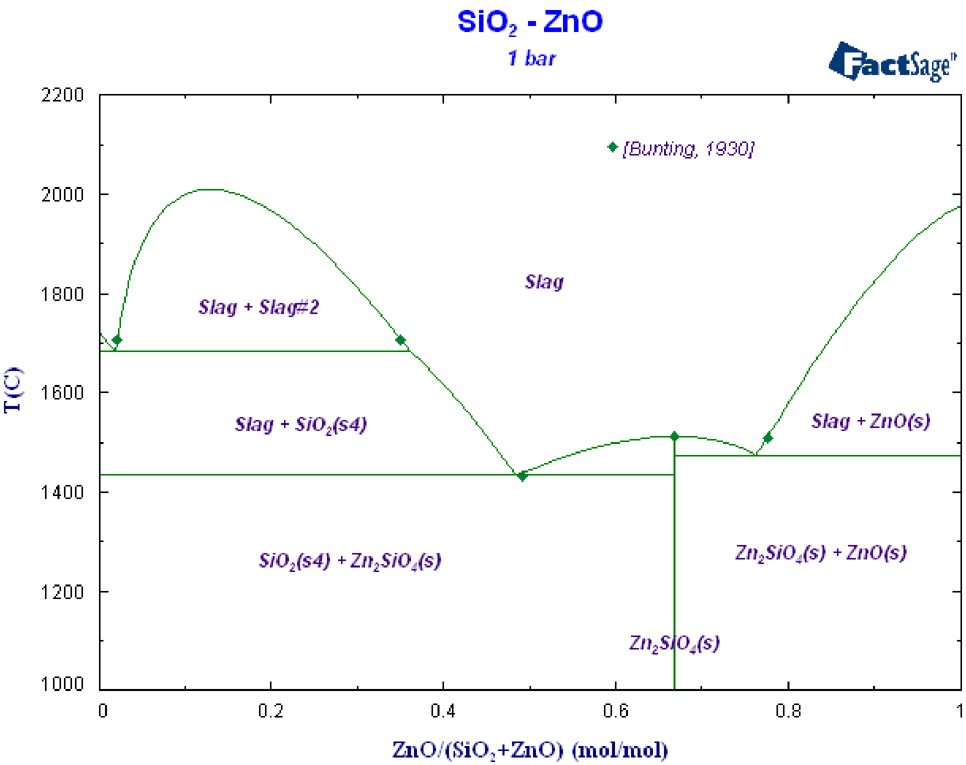


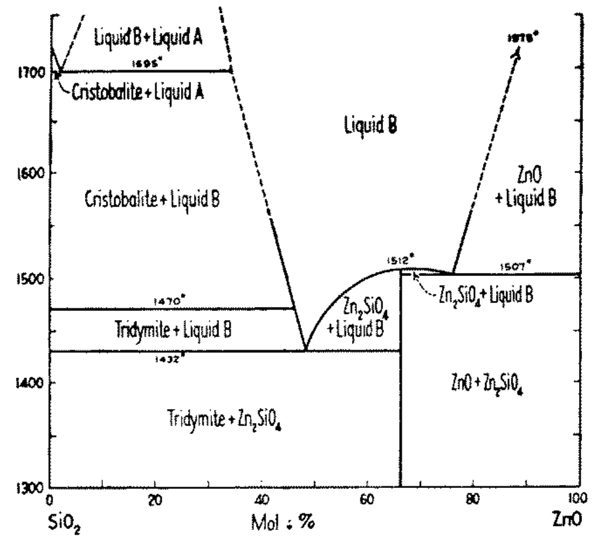


F.L. Katnack, F.A. Hummel, J. Electrochem. Soc., 105 [3], (1958), pp.125-133.



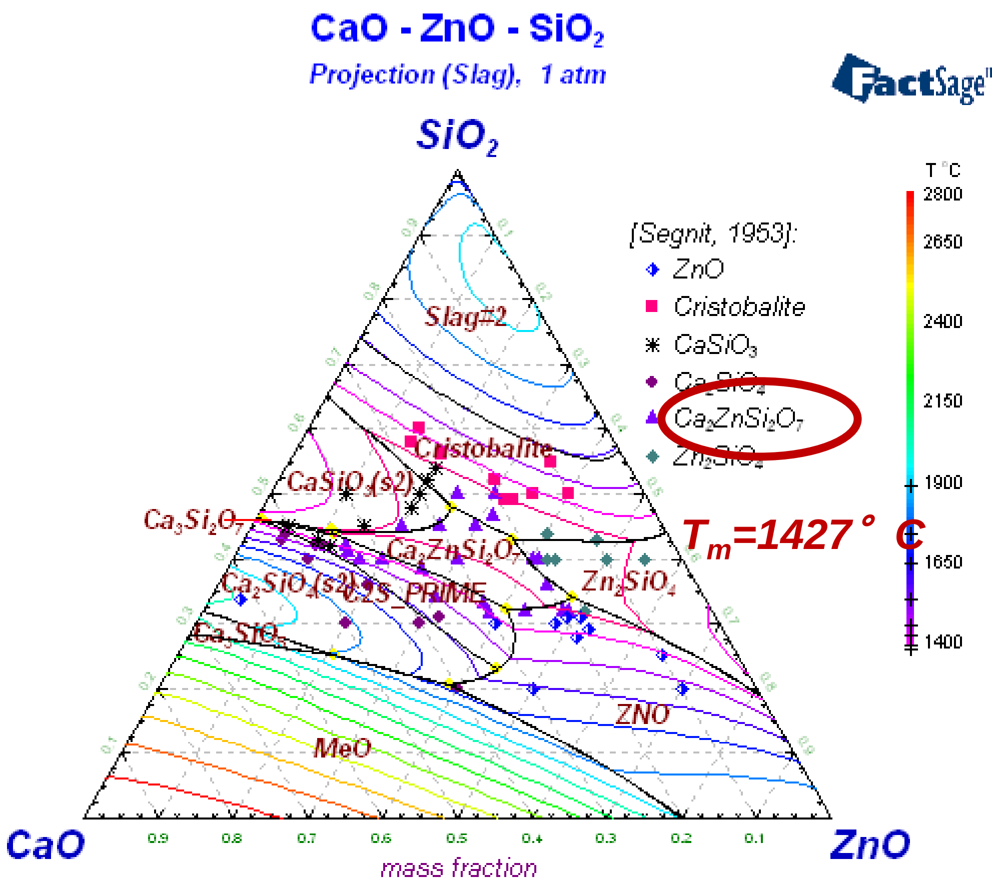
SiO_2–ZnO phase diagram

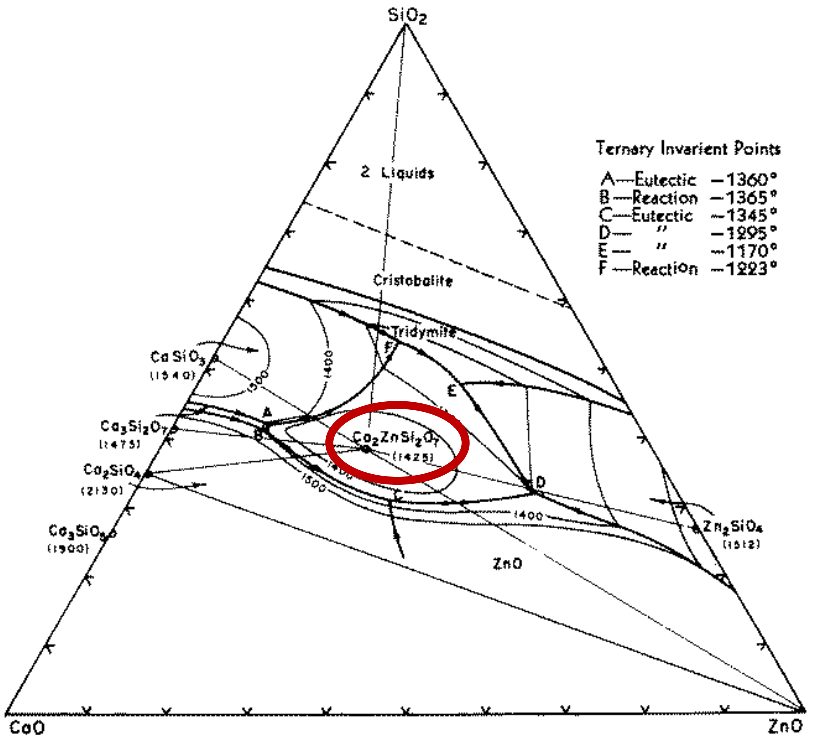




E.Bunting, J. Am. Ceram. Soc., 13 (1930), No.1, pp. 5-10.

Liquidus surface in CaO-SiO_2-ZnO

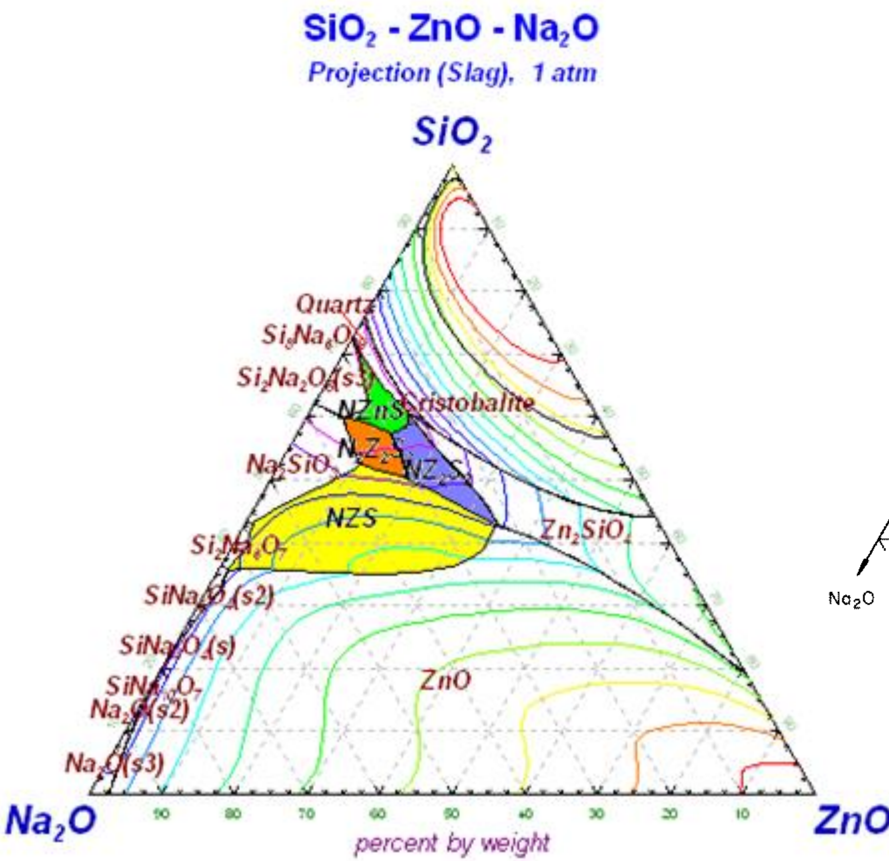


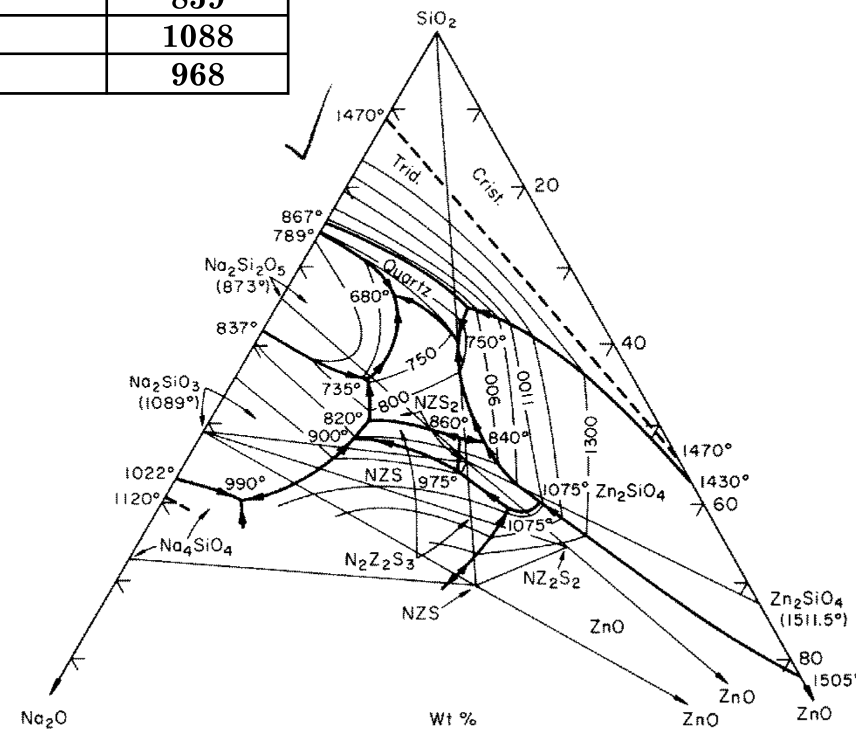


E. R. Segnit, J. Am. Ceram. Soc., 37[6], pp. 273-277 (1954).

Liquidus surface in Na_2O-SiO_2-ZnO

Phase	Formula	Tm,°C [1966Holland]	Tm,calc.
NZS	Na_2ZnSiO_4	1340	1339
NZS2	$Na_2ZnSi_2O_6$	860	859
NZ2S2	$Na_2Zn_2Si_2O_7$	1090	1088
N2Z2S3	$Na_4Zn_2Si_3O_{10}$	975	968





A.E. Holland. E.R. Segnit, Aust. J. Chem., 19 [6], (1966), pp. 905-913.

Isothermal sections in Na_2O-SiO_2-ZnO

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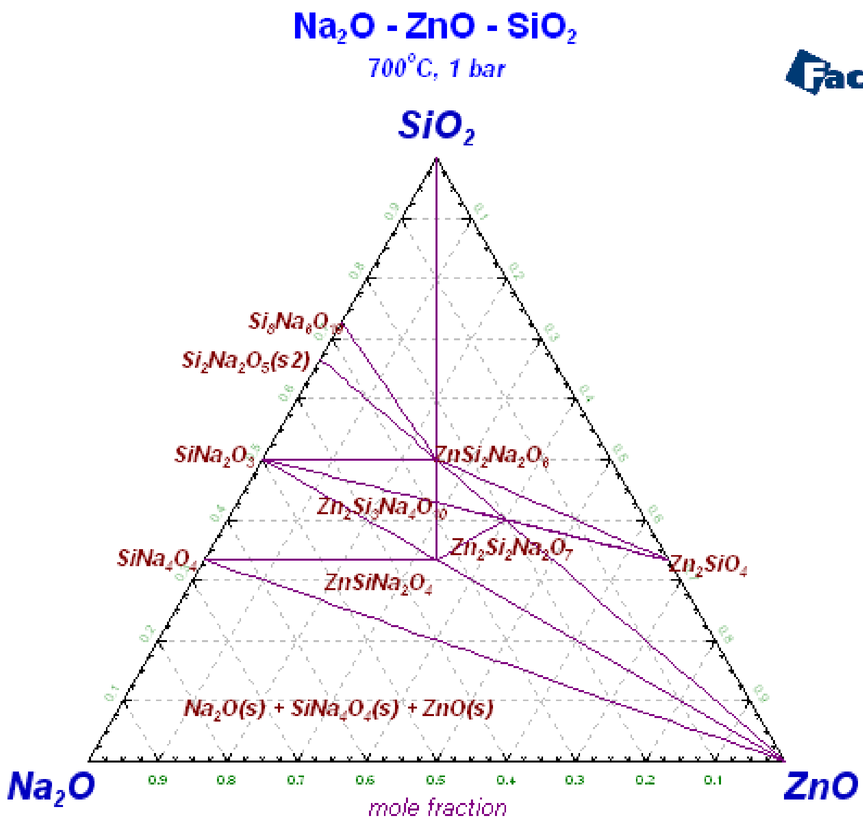
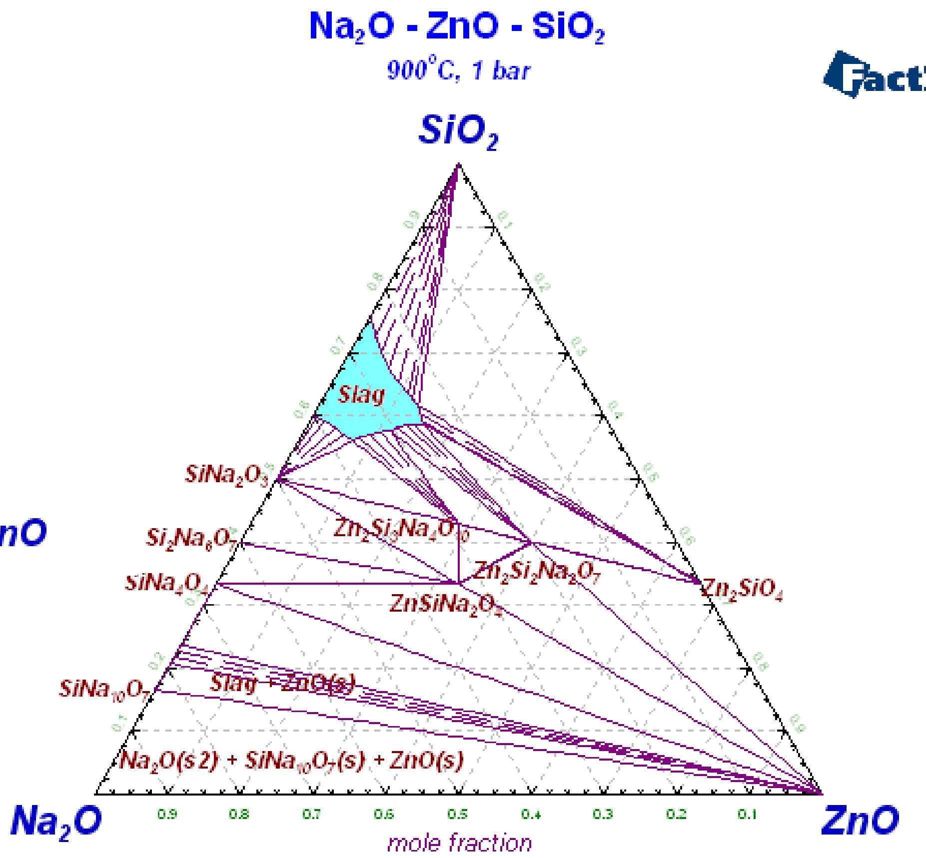
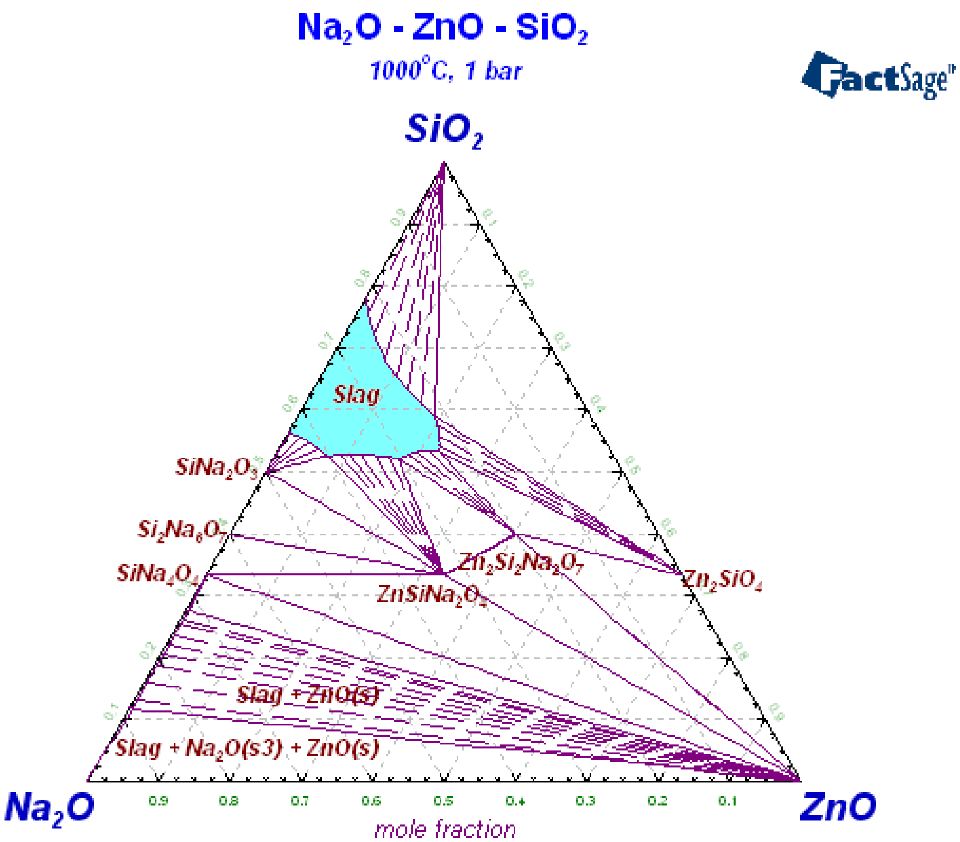
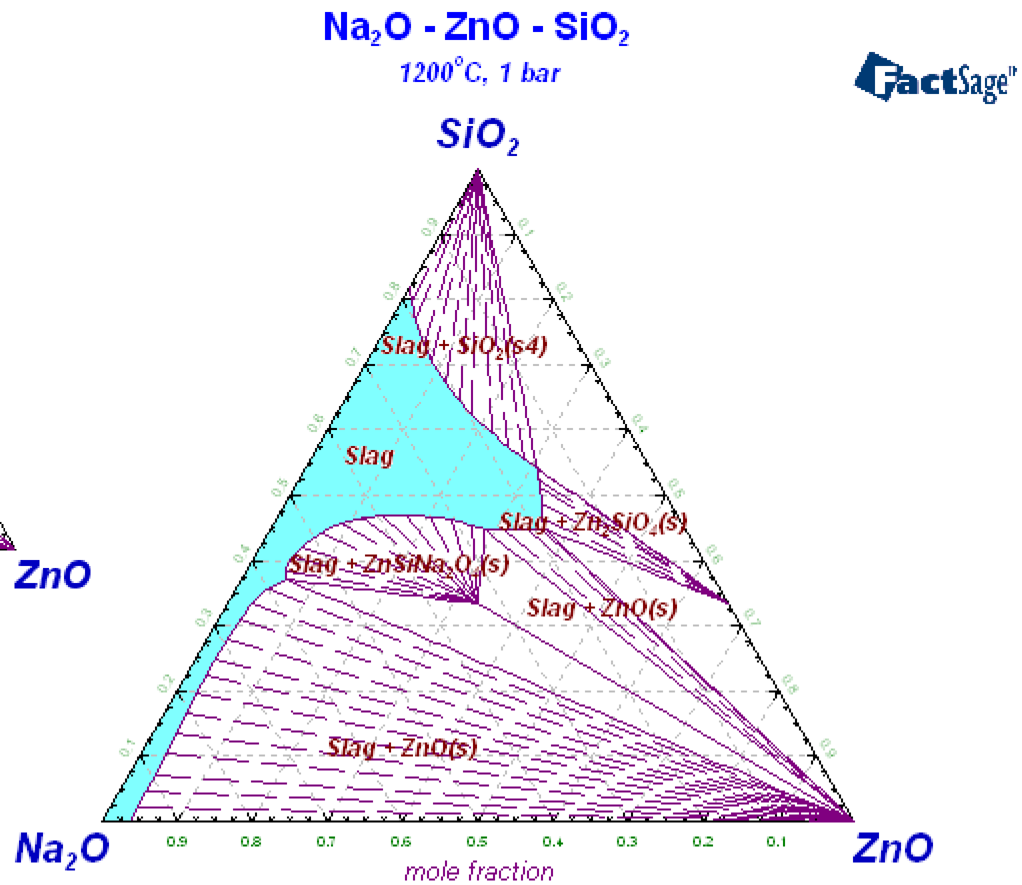




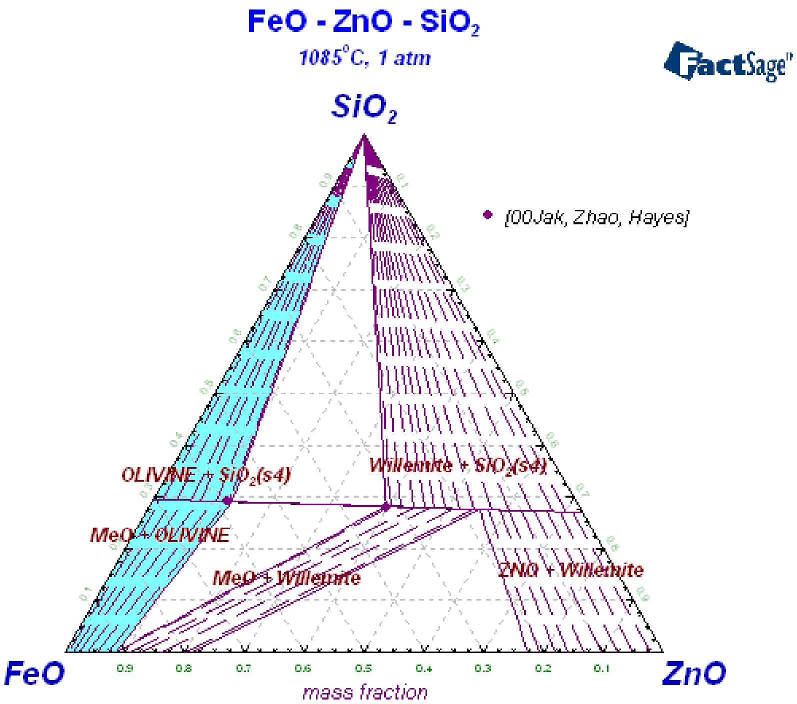
Isothermal sections in Na_2O-SiO_2-ZnO

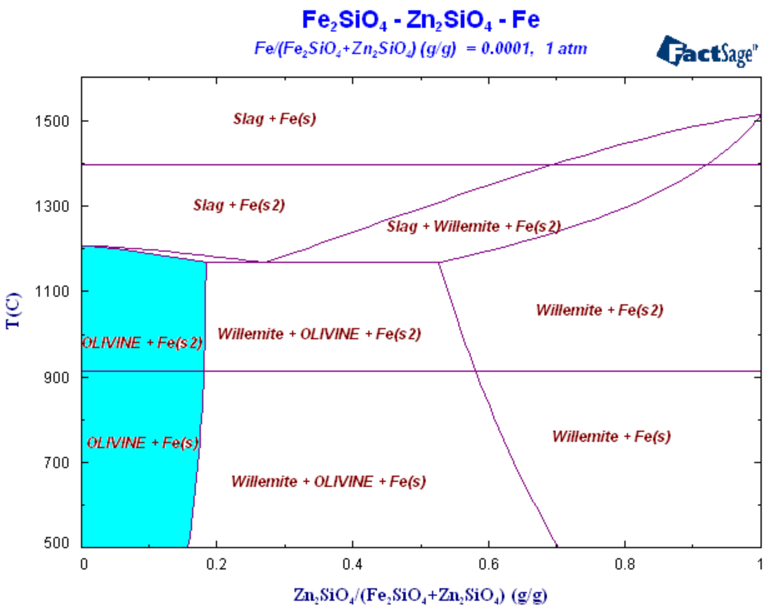




Olivine in $FeO\text{-}ZnO\text{-}SiO_2$

Olivine *$(Ca^{+2}, Fe^{+2}, Mg^{+2}, Mn^{+2}, Zn^{+2})(Ca^{+2}, Fe^{+2}, Mg^{+2}, Mn^{+2})(Si^{+4})(O^{-2})_4$*





Liquidus surface in FeO-SiO_2-ZnO

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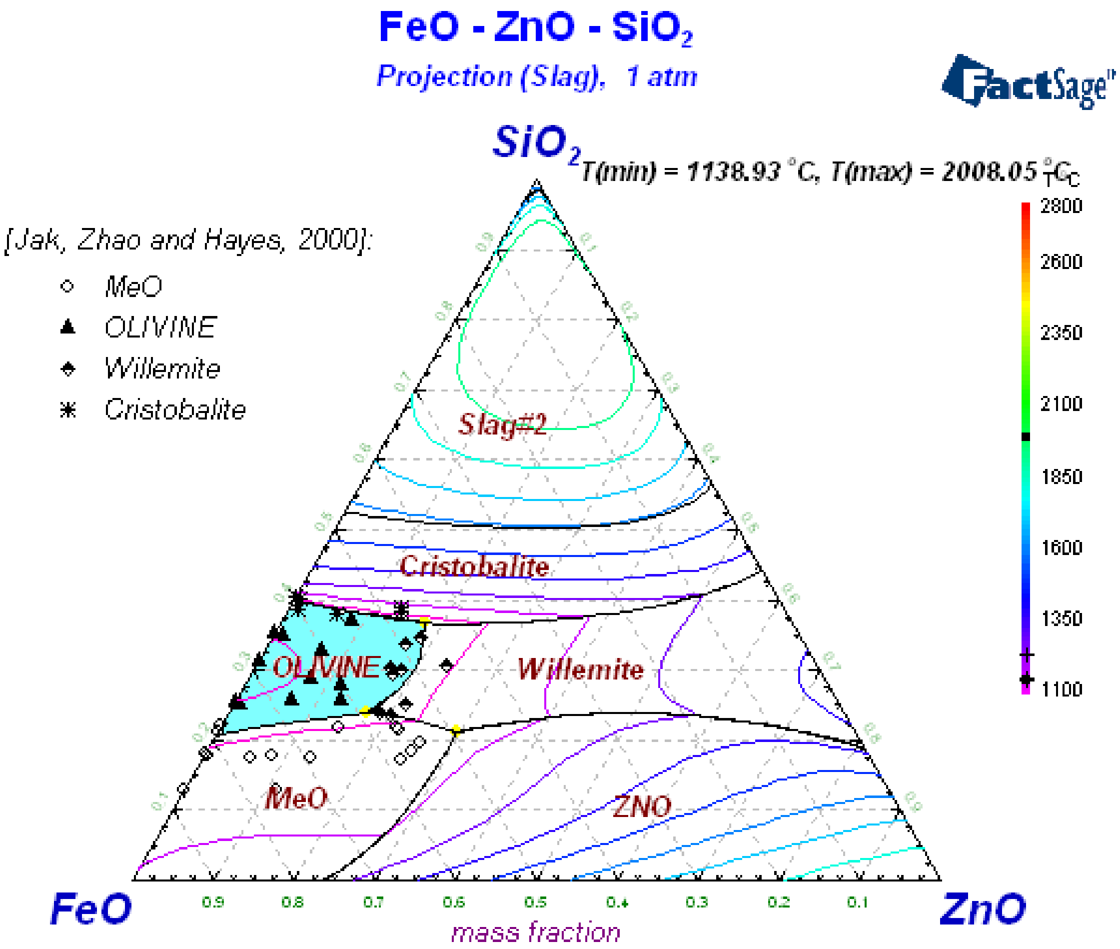
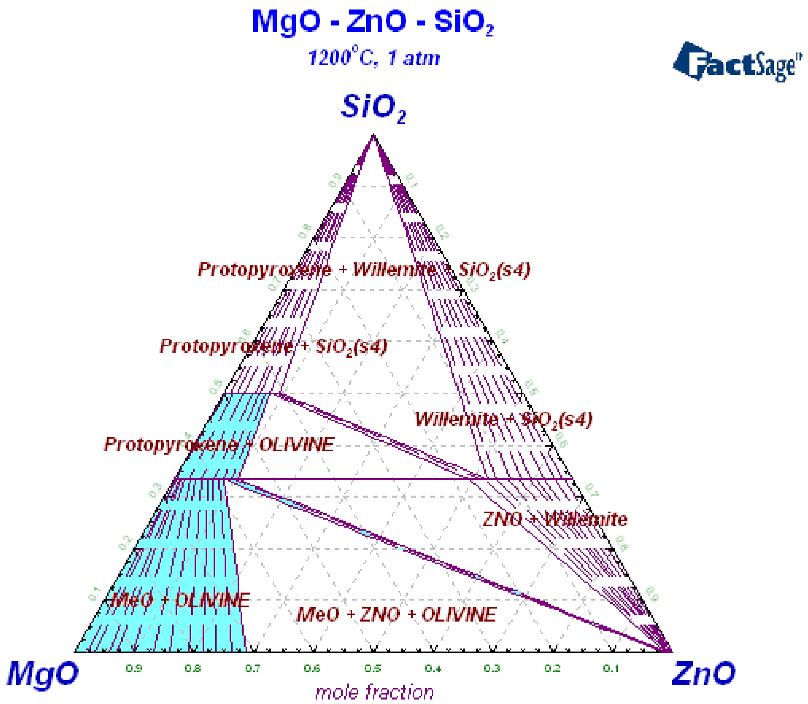
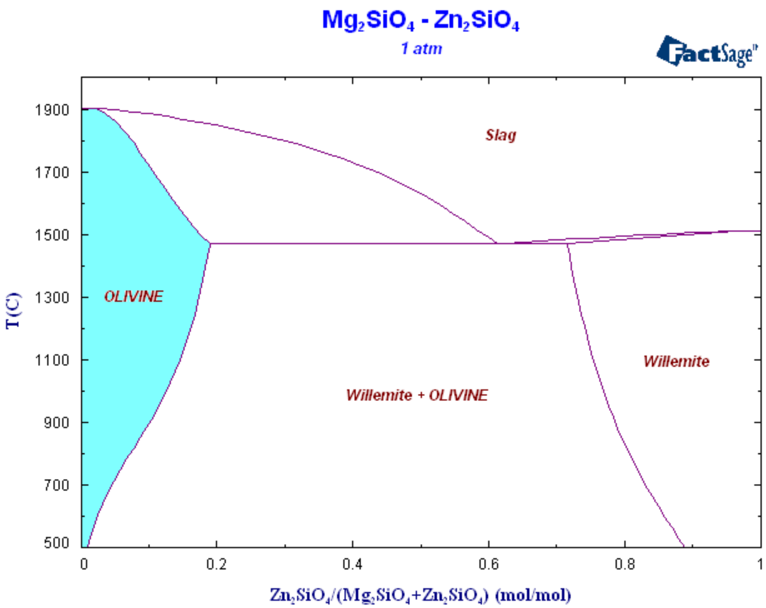


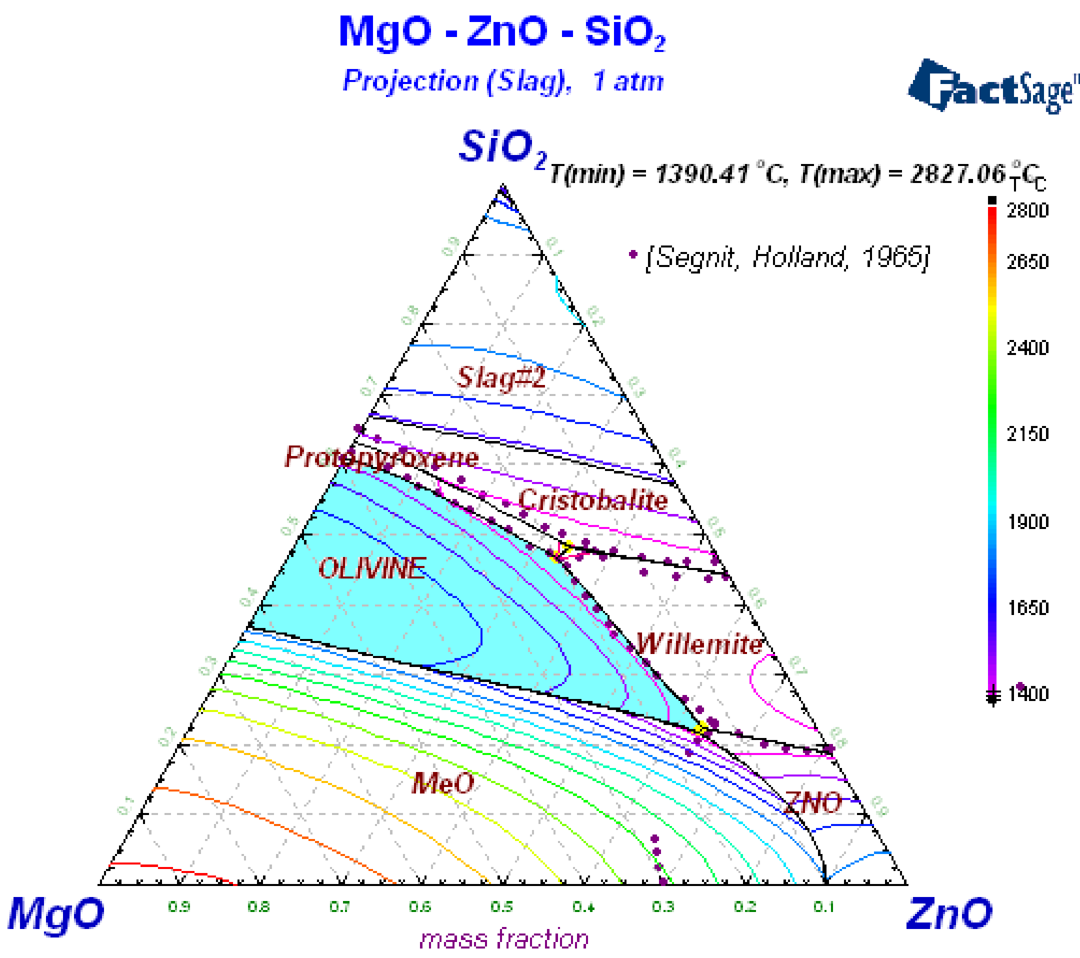
Olivine in MgO-ZnO-SiO_2

Olivine $(Mg^{+2},Zn^{+2})(Mg^{+2})(Si^{+4})(O^{-2})_4$



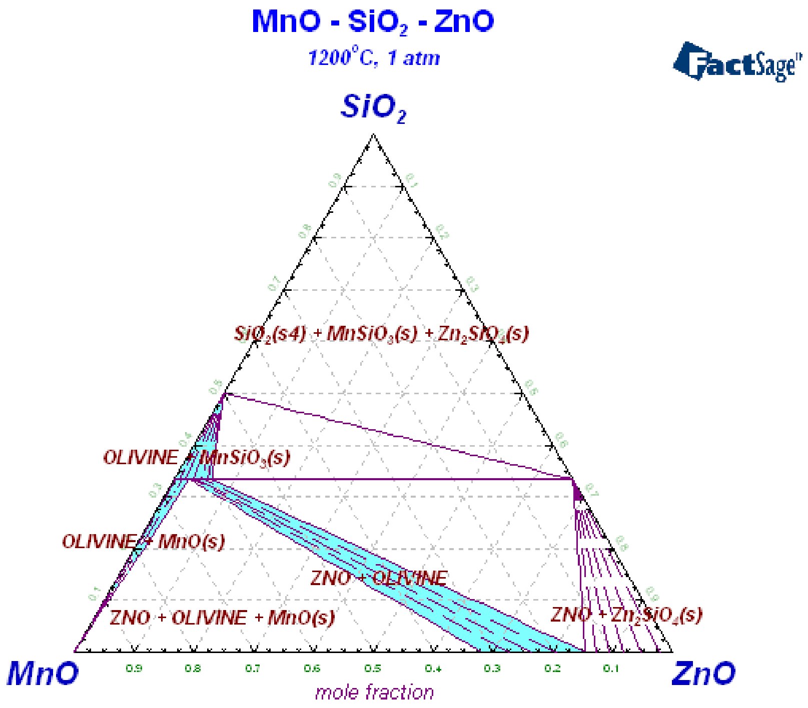


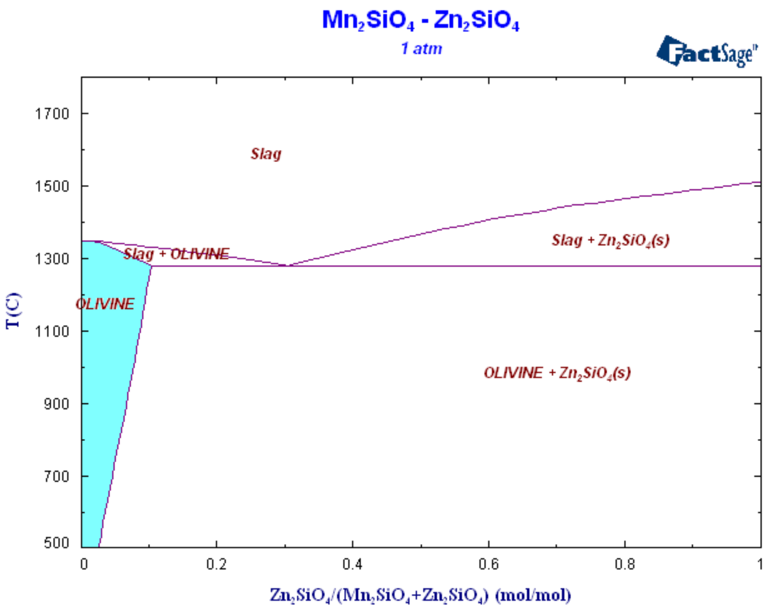
Liquidus surface in $MgO-SiO_2-ZnO$



Olivine in MnO-ZnO-SiO_2

Olivine $(Mn^{+2},Zn^{+2})(Mn^{+2})(Si^{+4})(O^{-2})_4$





Conclusions

- The liquid phase in all subsystems was evaluated using associate species model,
- All systems were assessed using experimental phase diagram information.
- ZnO has so far been integrated into the system CaO-MgO-Al_2O_3-CrO_x-MnO_x-FeO_x-K_2O-Na_2O-SiO_2-P_2O_5. All binary and 5 ternary systems were described.
- The solubility ranges of 8 solid solution phases containing Zn such as MeO, Zincite, Cubic-Spinel, Tetragonal-Spinel, Olivine, Protopyroxene, Willemite and α'–Ca_2SiO_4 were described using the sublattice model.

Future developments

Ternaries with ***ZnO*** and HotVeGas Oxide Database

Al_2O_3-CaO-CrO_x-FeO_x-K_2O-MgO-MnO-Na_2O-SiO_2

Thanks for your attention !