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Thermodynamic properties of $CaO–MgO–Al_2O_3$ melts

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Thermodynamic properties of melts and compounds of the $CaO–MgO–Al_2O_3$ system being a component of the $CaO–MgO–Al_2O_3–FeO–SiO_2$ system are of great importance for understanding and simulation of geochemical and cosmochemical phenomena connected to substance formation of Earth and Universe. The information on structure and properties of compounds and phase relations in considered system is poor [*Hallstedt*, 1992; *Hallstedt*, 1995].

This investigation presents the calculation of thermodynamic properties of the $CaO–MgO–Al_2O_3$ system melts at temperatures from 1800 to 2200 K in framework of the ideal associated solutions theory. The simplified lattice model, as before for the $CaO–Al_2O_3–SiO_2$ [*Shornikov*, 2007] and the $MgO–Al_2O_3–SiO_2$ [*Shornikov*, 2008] systems, accounts for the intermolecular interactions using the semi-phenomenological parameters, which were determined on the base of the experimental [*Allibert et al*., 1979; *Shornikov et al.*, 1997] and reference [*Glushko et al.,* 1978–1982] thermodynamic data. The source thermodynamic data considered 18 condensed phases (11 solid and 7 liquid) and 14 gas species; these components are listed in the Table 1. The solid solution field of spinel was taken into account in accordance with the experimental data obtained by mass-spectrometric Knudsen method [*Shornikov*, 2002].

Table 1. The Gibbs energies of formation (from elements) of condensed phases and vapor species over the $CaO–MgO–Al_2O_3$ system at 1960 K calculated in the present study according to data [*Glushko et al.,* 1978–1982; *Allibert et al*., 1979; *Shornikov et al.*, 1997]

Condensed phases				Gas phase	
Solid phases	$\Delta_f G°_{1960}$, kJ/mole	Liquid phases	$\Delta_f G°_{1960}$, kJ/mole	Vapor species	$\Delta_f G°_{1960}$, kJ/mole
Al_2O_3	–1046.788	Al_2O_3	–1029.796	Al	89.605
CaO	–425.847	CaO	–413.472	AlO	–72.492
$CaAl_2O_4$	–1533.967	$CaAl_2O_4$	–1536.789	AlO_2	–99.299
$CaAl_4O_7$	–2596.897			Al_2	196.232
$CaAl_{12}O_{19}$	–6795.323			Al_2O	–280.491
$Ca_3Al_2O_6$	–2400.664			Al_2O_2	–387.192
$Ca_5Al_6O_{14}$	–5489.050			Al_2O_3	–407.794
$Ca_{12}Al_{14}O_{33}$	–12932.929	$Ca_{12}Al_{14}O_{33}$	–13005.601	Ca	–17.589
$Ca_3MgAl_4O_{10}$	–3885.890	$Ca_3MgAl_4O_{10}$	–3885.257	CaO	–72.634
$MgAl_2O_4$	–1471.685	$MgAl_2O_4$	–1434.364	Mg	–53.734
MgO	–381.143	MgO	–359.587	MgO	–106.108
				O	124.333
				O_2	0.000
				O_3	271.522

The same Table 1 gives the calculated values of the Gibbs formation energies from elements ($\Delta_f G°_T$) for the compounds and the vapor species over the $CaO–MgO–Al_2O_3$ system. They were used for the calculation of the equilibrium conditions in the system at a given composition and temperature. The required equation solution for the integral Gibbs energy for the system studied was found by the widely used approach, namely the Gibbs energy minimization method.

The oxide activities $a(i)$ and the Gibbs energy of melt formation (from oxides) in the $CaO–MgO–Al_2O_3$ system ($\Delta_f G_T$) were calculated at fixed weight concentration of MgO, equal to 7.16 wt. % (Table 2).

Table 2. The investigated compositions of the $CaO–MgO–Al_2O_3$ system

No.	Concentration, wt. %			Concentration, mole %		
	CaO	MgO	Al_2O_3	CaO	MgO	Al_2O_3
1	52.84	7.16	40.00	59.48	15.76	24.76
2	50.24	7.16	42.60	57.31	15.97	26.73
3	47.64	7.16	45.20	55.07	16.19	28.74
4	45.04	7.16	47.80	52.78	16.41	30.81
5	41.98	7.16	50.86	50.00	16.68	33.32
6	39.38	7.16	53.46	47.57	16.91	35.52
7	36.78	7.16	56.06	45.07	17.15	37.78
8	34.18	7.16	58.66	42.49	17.40	40.11
9	31.58	7.16	61.26	39.84	17.66	42.50
10	28.98	7.16	63.86	37.10	17.93	44.97
11	26.38	7.16	66.46	34.29	18.20	47.51
12	23.91	7.16	68.93	31.53	18.46	50.00

The obtained results are in Figure 1 in comparison with experimental [*Allibert et al*., 1979] and calculated [*Hallstedt*, 1992] data.

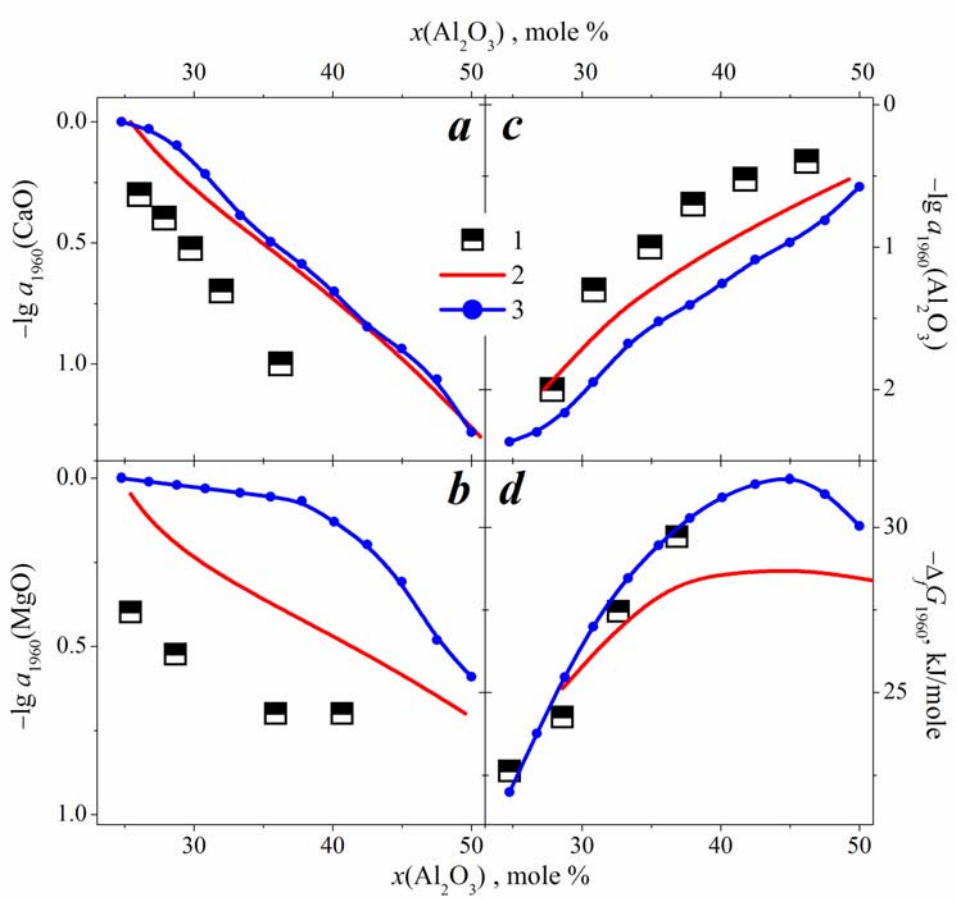

Fig. 1. The activities of oxides (*a*-*c*) and the Gibbs energy of formation from oxides (*d*) of the $CaO–MgO–Al_2O_3$ system melt at the temperature 1960 K: 1 – obtained by mass-spectrometric Knudsen effusion method [*Allibert et al*., 1979], 2 – calculated according to the sublattice model [*Hallstedt*, 1992] and 3 – calculated in the present study.

As seen from the Fig. 1 the calculated oxide activities and the Gibbs energy of melt formation (from oxides) in the $CaO–MgO–Al_2O_3$ system melts obtained at present study satisfactory correspond

to experimental as well as theoretical data. Observable deviations of the calculated values of activities *a*(MgO) from experimental data (Fig. 1*b*) are insignificant – approximately in 2 times. The minimal value of the Gibbs energy of melt formation (from oxides) in the $CaO–MgO–Al_2O_3$ system is not large ($\Delta_f G_{1960}$ = –31.5 kJ/mole). It corresponds to the composition containing 45 mole % Al_2O_3 closed to liquidus line. It shown the instability in melt of the ternary compound $Ca_3MgAl_4O_{10}$ containing 33.3 mole % Al_2O_3 (Fig. 1*d*).

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