1.5.P04

Internally consistent thermodynamic data for high-pressure phases in the system CaO-MgO-Al$_2$O$_3$-SiO$_2$-H$_2$O

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In order to enable reliable calculations of phase relations among high-pressure phases the Berman [1] data set was augmented by data for the high-pressure phases stishovite (stv), topaz-OH (toz-OH), phase pi (pi), Mg-staurolite (Mg-st), Mg-sursassite (MG-sur), and Mg-chloritoid (Mg-cld) using a similar optimization technique as described by Berman et al. [2]. The data of several other phases of the system CaO-MgO-Al$_2$O$_3$-SiO$_2$-H$_2$O obtained in the Berman data base were slightly refined to keep the consistency to the reversal brackets and the originally measured data: andalusite (and), clinochlore (chl), coesite (cs), diaspore (dsp), kaolinite (kln), kyanite (ky), lawsonite (lws), pyrophyllite (prl), sillimanite (sil), zoisite (zo). C$_P$-data were kept constant [1] or estimated [3].

	$\Delta_f H^0_{298}$ kJ mol^{-1}	S^0_{298} J K^{-1} mol^{-1}	V^0_{298} J K^{-1} mol^{-1}	$v_1 \cdot 10^5$ bar^{-1}	$v_2 \cdot 10^{12}$ bar^{-2}	$v_3 \cdot 10^5$ K^{-1}	$v_4 \cdot 10^8$ K^{-2}
and	−2589.857	91.47	5.146	−0.0653		2.291	0.170
chl	−8902.557	438.59	21.000	−0.1328	3.840	2.114	0.939
Mg-cld	−3557.515	131.74	6.874	−0.0692		2.549	
cs	−907.509	39.63	2.064	−0.0998	1.823	0.620	0.960
dsp	−999.115	35.22	1.776	−0.0719	0.629	3.244	0.685
kln	−4119.400	204.18	9.952	−0.1200		3.200	
ky	−2593.767	82.71	4.408	−0.0593	1.021	1.732	0.788
lws	−4866.666	228.04	10.155	−0.0825		3.339	
Mg-sur	−13908.684	606.86	26.888	−0.0826	0.919	3.175	0.087
pi	−9586.755	403.21	18.559	−0.0678		2.255	
prl	−5640.502	239.43	12.782	−0.1800		2.621	
sil	−2586.169	95.40	4.984	−0.0601	1.341	1.138	0.605
Mg-st	−24997.390	945.25	44.260	−0.0579		2.012	
stv	−870.860	25.59	1.401	−0.0318		1.849	
toz-OH	−2885.927	117.38	5.352	−0.0630		1.938	
zo	−6889.494	297.20	13.588	−0.0695		2.752	

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1.5.P05

Role of internal pressure in a ferroelastic phase transition

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It is shown that the internal pressure may be represented as driving force for the proper ferroelastic phase transitions (FPTs) induced by cation exchange. It has been found that the internal stress tensor, generated by the cation exchange, is of a more complicated nature than the tensor of the external stress. This difference comes from a specific coupling of the substituting cations with local, microscopic displacements of the neighbouring atoms inside the unit cell. It becomes evident why in a number of experiments a significant difference in the action of internal and external pressures on the crystal structure is observed and, also, why the internal pressure causes a greater anisotropy than the external one. An equation has been obtained, with the help of which it appears possible to predict the internal pressure of the proper monoclinic-triclinic ferroelastic phase transition induced by cation exchange if the initial effective elastic moduli are known.

In the previous work [1], using the "ball-and-perfect springs" model, we have determined the mechanism of occurrence of a soft mode at a proper FPT in Sr-anorthite (Sr,Ca)Al$_2$Si$_2$O$_8$ and some other crystals under the external pressure. In the present work, we consider the same FPT induced by Ca and Sr cation exchange rather than by the external pressure. In other words, the same approach is used for the case of the internal (chemical) pressure. We have considered the origin of the internal pressure in the process of the cation exchange [2]. We have given the following definition of the internal pressure: "internal pressure due to the concentration N of new ions is equal to such an external pressure which at the presence of additional forces on atoms $\mathbf{f_x}$ would result in the same macroscopic deformation as does the concentration N". Thus, the macroscopic strain is partly a secondary effect of the cations exchange, whereas it is a primary effect of an external stress.

References
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