Immiscibility and critical points in titanite solid solutions: The binaries CaTiOSiO$_4$-CaSnOSiO$_4$ and CaTiOSiO$_4$–CaSiOSiO$_4$.

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Introduction: Since the early seminal papers [e.g., 1, 2] that mostly dealt with end-member titanite crystal chemistry there has been significant progress in better understanding the crystal chemistry and phase transitions of end-member titanite [e.g., 3, 4, 5], titanite-like compounds and solid solutions [6, 7, 8] whether natural or synthetic. A much smaller group of studies have focused on the structural properties – phase equilibria of titanite solid solutions [9, 10, 11] and none on titanite liquid solutions. Here I apply a simple phenomenological model [12] that relates elastic contributions to strain energy under the assumption of perfect and isotropic elasticity. Subsequently, I derive the excess thermodynamic properties of titanite solid solutions and discuss the results of the computations relative to relevant experimental data.

Discussion: For the CaTiOSiO$_4$ – CaSnOSiO$_4$ and CaTiOSiO$_4$ – CaSiOSiO$_4$ binaries the elastic contribution to strain energy is estimated with the equation $U = 2 \cdot G_i \cdot C_i \cdot [\Delta V]^2 / 3 \cdot V_{o,i}$ where G_i is the shear modulus of component i, $V_{o,i}$ is the component i unit cell or molar volume, ΔV is the volume difference between the solid solution components, K_i is the bulk modulus of component i, and the quantity $C_i = 3 \cdot K_i / (3 \cdot K_i + 4 \cdot G_i)$. The bulk and shear modulus are related through the equation $G = 3 \cdot (1-2v) \cdot K / (2(1+v))$ for isotropic materials and for a Poisson's ratio v value of 0.15, because calculations with v between 0 and 0.4 showed no measurable effects. [7, 13, 14] were the source for bulk modulus K_o & K' values for A2/a CaTiOSiO$_4$, CaSnOSiO$_4$, and CaSiOSiO$_4$. Model excess thermodynamic properties of mixing

were calculated as follows:

$$U^E = x_1 \cdot x_2^2 \cdot U_{12} + x_1^2 \cdot x_2 \cdot U_{21}$$

$$H^E = U^E + P \cdot V^E$$

$$G^E = H^E - T \cdot S_{config}$$

The initial assumption was that $U_{12} \neq U_{21}$ and let the data dictate whether the binary is "symmetric" or "asymmetric".

On the basis of low-pressure hydrothermal experiments [15] proposed the existence of an asymmetric miscibility gap with a critical temperature and composition of T_c = 615 ºC and X_c = CaTi$_{0.75}$Sn$_{0.25}$OSiO$_4$. However, the measured excess volume of mixing is zero [16] and in the course of studying the CaTiOSiO$_4$–CaSnOSiO$_4$ binary, [17] experimentally concluded that if the miscibility gap exists at all then the critical temperature has to be much lower than 615 ºC. In the CaTiOSiO$_4$–CaSiOSiO$_4$ binary the isothermal experiments of [18] suggest the possibility of immiscibility at 1350 ºC and near 8.5 GPa. The data [18] also indicate that Si-rich titanite is unstable with respect to Ca- and Si-rich phases such as *Wo*, *Pv*, and *Stish*.

It is clear that if these binaries are characterized by miscibility gaps then the excess enthalpies have to be positive (H^E >0) and exceed significantly the contribution of configurational entropy to promote unmixing. Furthermore, the model activities in phase equilibria have to account for non-ideality. Note that in both binaries the experimentally determined excess volume [16, 18] and the excess enthalpy of mixing [19] are zero.

In both binaries the model excess enthalpies are always positive and practically zero and agree with the experimental data which imply ideal mixing. I, therefore, conclude that the CaTiOSiO$_4$–CaSnOSiO$_4$ and CaTiOSiO$_4$–CaSiOSiO$_4$ binaries are not characterized by immiscibility. Furthermore, the experimental data for Sn-titanite solutions [15] and Si-rich titanite solutions [18] likely reflect the metastable nature of the starting materials, i.e., gels and glasses. Both data sets should be best considered as synthesis and not phase equilibrium experiments. Finally, ideal activity models for Sn- and Si-rich titanite in phase equilibrium calculations should suffice.

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