

A simulation study on mixing thermodynamics of rutile-cassiterite solid solution

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Modern computer simulation tools make it feasible to study solid solutions at the atomistic level and thus to contribute to the understanding of their structural and thermodynamic properties. Here we investigate the thermodynamical mixing functions of the rutile - cassiterite (TiO_2 - SnO_2) solid solution based on first principles computation of local interactions between Sn and Ti.

Several different computational schemes were tested and compared. Direct DFT calculation of the partition function was carried out within a $2 \times 2 \times 2$ supercell of rutile. Further, pairwise interactions were computed within a $2 \times 2 \times 4$ supercell and a generalised Ising model expansion was employed for the calculation of the energies of all possible configurations. The Gibbs free energy was modelled both via a direct calculation of the partition function within a $2 \times 2 \times 4$ supercell and via a Monte Carlo simulation of a $8 \times 12 \times 16$ supercell. Quasi-random structures and empirical pair potentials were used to assess the excess vibrational free energy contribution. Consequently, the phase diagram has been outlined and compared to the experimental data.

The phase relations derived from Monte Carlo simulations with a correction for the excess vibrational entropy are in good agreement with the available experimental data [1]. The direct calculation of the partition function for a $2 \times 2 \times 4$ supercell can provide reasonable phase relations only when the configurational entropy is corrected to provide consistency with the ideal mixing in the high-temperature limit.

[1] Naidu & Virkar (1998) *J. Am. Ceram. Soc.* **81**, 2176-2180.