



Atomistic simulation of local structure and mixing properties of mineral solid solutions

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At present there are several ways to simulate solid solution structure and properties by using ab initio as well as semi-empirical (atomistic) approaches [1]. The main problem of each approach is a reasonable representation of random distribution of atoms substituting each other over common positions. A procedure in operation here used large supercells and generation of most disordered atomic configurations for some selected compositions of solid solution (1:1, 1:3, 3:1, 4:1, 1:4, etc.). The following binary systems were studied by such a way: NaCl – KCl [2, 3, 4], CaO – MgO, CaO – SrO, SrO – BaO (supercell $4 \times 4 \times 4$, 512 atoms) [3], TiO₂ – SnO₂ ($4 \times 4 \times 4$, 384 atoms), Al₂O₃ – Cr₂O₃, Al₂O₃ – Fe₂O₃, Fe₂O₃ – Cr₂O₃ ($4 \times 4 \times 4$, 480 atoms) [5]. The calculation technique was based on the method of semi-empirical potentials using the GULP program [6]. Potential parameters of ionic (halides) or partially covalent (oxides) interatomic interactions were optimized by using of structural, thermodynamic and elastic properties of pure components. Calculated heat capacities and entropies as a function of temperature were in a good agreement with experimental data. Excess mixing properties (enthalpy, volume, bulk modulus, vibrational entropy) were calculated for different compositions of the solid solutions. This allowed to reproduce Gibbs energy as a function of temperature and composition and estimate critical temperature of decomposition and miscibility gap of a solid solution. Statistical analysis of bond lengths frequencies for the nearest and next-nearest neighbors in (Na_{0.5}K_{0.5})Cl, (Ca_{0.5}Mg_{0.5})O, (Ti_{0.5}Sn_{0.5})O₂, (Al_{1.0}Cr_{1.0})O₃ solid solutions revealed a detailed picture of the lattice relaxation. These results were compared with earlier predictions made by phenomenological crystal chemical models [7, 8] and available EXAFS data.

References

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