Research project P23056-N21 funded by FWF

Excess heat capacity of low structural state feldspars

Status finished

Project leader Benisek Artur

The most important results of this project come from the investigations and explanations of the vibrational behaviour of the atoms in solid solutions. The frequencies of the atomic vibrations are often strongly affected by the solid-solution process giving rise to excess vibrational entropies, which are deviations of the vibrational entropy from ideal behaviour. They stabilise (if positive) or destabilise (if negative) these materials and thus play an important role for phase-stability calculations. The vibrational entropies of some solid-solution series were investigated experimentally and by quantum-mechanical calculations. These investigations contributed to the understanding of the vibrational entropy from a macroscopic point of view but also towards an atomic-level understanding. It could be shown that the differences of elasticity of the components building the solid solution are responsible for generating positive or negative deviations from ideal vibrational behaviour. An empirical equation for estimating the excess vibrational entropy, established in a preliminary project, was improved in the course of this project. It can now be applied to several classes of materials, i.e., silicates, chlorides, and metallic alloys.

We examined the vibrational entropies of the alkali feldspars, plagioclases, garnets and chlorides as well as silver-palladium, platinum-rhodium, copper-zinc, and copper-gold solid solutions. These investigations brought not only insight into the physics of the vibrational behaviour of the atoms in solid solutions, but they also improved the thermodynamic description of these materials significantly. Beside the research on solid solutions, the determination of the standard entropy of different mineral end-members contributed also to the improvement of the thermodynamic data basis. The investigations on stishovite, dmitryivanovite, TiO_2II, starkeyite, almandine, grossular und hydrogrossular are to be mentioned in this context.

In addition to the goals of the project, an experimental method for determining the configurational entropy (coming from the disorder of the atomic distribution) was developed by comparing calorimetrically based data with data from phase-equilibrium experiments. The differences could be used to extract the configurational entropy of some solid solutions.

Peer-reviewed publications

Benisek A., Dachs E., Grodzicki M. (2015) First-principles investigation of the lattice vibrations in the alkali feldspar solid solution. Phys Chem Minerals 42, 243-249. Link to Open Access Paper

Benisek A., Dachs E. (2015) The vibrational and configurational entropy of disordering in Cu_3Au. J Alloys Compounds 632, 585-590. Link to Open Access Paper

Dachs E., Geiger CA., Benisek A. (2014) Thermodynamic mixing properties and behavior of grossular-spessartine, $(Ca_xMn_{1-x})_3Al_2Si_3O_{12}$, solid solutions. Geochim Cosmochim Acta 141, 294-302. Link to paper

Link to accepted manuscript

Benisek A., Dachs E., Salihovic M., Paunovic A., Maier ME. (2014) The vibrational and configurational entropy of α-brass. J Chem Thermodynamics 71, 126-132.

Link to Open Access Paper

Yong W., Dachs E., Benisek A., Secco RA., (2014) Heat capacity and entropy of rutile and TiO_2II: Thermodynamic calculation of rutile – TiO_2II transition boundary. Phys Earth Planetary Int 226, 39-47. Link to paper

Link to accepted manuscript

Benisek A., Dachs E., Kroll H. (2014) Thermochemistry of the alkali feldspars: Calorimetric study of the entropy relations in the low albite – low microcline series. American Mineralogist 99, 76-83. Link to paper

Link to accepted manuscript

Dachs E., Geiger CA., Benisek A., Grodzicki M. (2013) Thermodynamic mixing properties and behavior of almandine-spessartine solid solutions. Geochim Cosmochim Acta 125, 210-224.

Link to paper

Link to accepted manuscript

Benisek A., Dachs E. (2013) Calorimetric study of the entropy relation in the NaCl-KCl system. J Chem Thermodynamics 62, 231-235.

Link to Open Access Paper

Benisek A., Dachs E., Carpenter M.A. (2013) Heat capacity and entropy of low structural state plagioclases. Phys Chem Minerals 40, 167-173.

Link to paper

Link to accepted manuscript

Grevel K-D., Majzlan J., Benisek A., Dachs E., Steiger M., Fortes A.D., Marler B. (2012) Experimentally determined standard thermodynamic properties of synthetic $MgSO_4{\cdot}4H_2O$ (Starkeyite) and $MgSO_4{\cdot}3H_2O$: A revised internally consistent thermodynamic data set for magnesium sulfate hydrates. Astrobiology 12 (11), 1042-1054.

Link to paper

Link to accepted manuscript

Dachs E., Geiger C.A., Benisek A. (2012) Almandine: Lattice and non-lattice heat capacity behavior and standard thermodynamic properties. American Mineralogist 97, 1771-1782.

Link to paper

Link to accepted manuscript

Dachs E., Geiger C.A., Benisek A., Grevel K-D. (2012) Grossular: A crystal-chemical, calorimetric, and thermodynamic study. American Mineralogist 97, 1299-1313.

Link to paper

Link to accepted manuscript

Geiger C.A., Dachs E., Benisek A. (2012) Thermodynamic behavior and properties of katoite (hydrogrossular): A calorimetric study. American Mineralogist 97, 1252-1255.

Link to paper

Link to accepted manuscript

Benisek A., Dachs E. (2012) A relationship to estimate the excess entropy of mixing: Application in silicate solid solutions and binary alloys. J Alloys Compounds 527, 127-131.

Link to Open Access Paper

Benisek A., Kroll H., Dachs E. (2012) The heat capacity of fayalite at high temperatures. American Mineralogist 97, 657-660.

Link to paper

Link to accepted manuscript

Yong W., Dachs E., Benisek A., Withers A.C., Secco R.A. (2012) Heat capacity, entropy, and phase equilibria of dmitryivanovite. Phys Chem Minerals 39, 259-267.

Link to paper

Link to accepted manuscript

Yong W., Dachs E., Benisek A., Secco R.A. (2012) Heat capacity, entropy and phase equilibria of stishovite. Phys Chem Minerals 39, 153-162.

Link to paper

Link to accepted manuscript

Dachs E., Benisek A. (2011) A sample-saving method for heat capacity measurements on powders using relaxation calorimetry. Cryogenics 51, 460-464.

Link to Open Access Paper